ROGERS'
INDUSTRIAL CHEMISTRY

A MANUAL FOR THE STUDENT AND MANUFACTURER

SIXTH EDITION—IN TWO VOLUMES

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PREFACE TO SIXTH EDITION

The First Edition of "Industrial Chemistry—A Manual for the Student and Manufacturer" in 1912, edited by Allen Rogers, was a landmark in the presentation of information about the then infant chemical industries. It received prompt recognition as the outstanding work in the field and it soon became second nature to "Look it up in Rogers."

Under Dr. Rogers' guidance, the succeeding four editions of the Manual expanded and kept pace with the growing industry, the last edition being in 1931. In 1938 the preparation of the Sixth Edition had been started. It was a very serious loss to the field of technical education that Dr. Rogers' death in that year cut off the work that would have been an invaluable heritage to American chemists and chemical engineers.

The past two decades have not only seen tremendous changes in the growth and scope of chemical industry but have witnessed a minor revolution in the approach and techniques of education in the field. When the present editor took over in 1940, it was decided that thorough revision and rewriting were called for. Increased emphasis should be given to the background knowledge of engineering and economics which is more or less common to all chemical industries and the interrelationships among the operations and processes of the different branches should be emphasized. In addition, completely new chemical industries and increased knowledge in all branches were making bids for ever-increasing space. The prospects were that the new edition would become encyclopedic in extent and thus defeat its purpose of being a book which would afford the student or manufacturer a rapid survey of the essential features of the most important branches of the industry. Consequently, the pruning operation had to be applied drastically, to make room for essential new material. Some of the chapters which appeared in the older editions have been removed; others have had many details eliminated, which would be of interest only to the specialist. To make up for this, emphasis has been placed upon the use of footnote references to original sources and upon more extensive classified bibliographies at the end of the chapters. It is hoped this will make the book useful as a reference work for those who wish to delve extensively into any of the fields which are covered.

The book has been divided into eight sections to emphasize the common background of the subject matter. The classification cannot be exact, but it is felt that it will help to keep the widely diversified material from seeming chaotic. Numerous cross references are given between chapters to help the reader find the information which is common to the different industries.

The potential audience of this book is visualized as any one with a knowledge of general chemistry, be he student, engineer, or executive, who wishes to grasp the essential features of the various branches of modern chemical industry. He will be taken on an extensive plant survey of an industry, have the essential operating features explained to him by a recognized authority in the field, and at the end of his visit be supplied with a comprehensive list of literature references for further detailed study.

Comments and suggestions from readers for improvement of future editions of the work will be received with genuine thanks.

Many of the old authors kindly consented to revise their material for the new edition and several new authors have been added. The editor wishes to take this space to express his gratitude to these forty-nine busy men who generously contributed their time to the preparation of the individual chapters.

C. C. FURNAS, *Editor.*

New York, N. Y.
August 1942

INTRODUCTION

Men have been harnessing chemical reactions ever since the members of some sub-human species learned to control fire. And before any histories were written, artisans unwittingly employed chemistry in the preparation of natural dye-stuffs, the making of leather, the brewing of pharmaceutical concoctions, the smelting of metallic ores, the making of alcoholic beverages. But all these early activities were highly empirical arts, shrouded in mystery. It was only a few generations ago that chemistry became something approaching an exact science. Even less time has elapsed since chemical industry began to be put on a scientific basis.

The effect of the impact of the new science on the old art has been phenomenal. When men began to understand molecules they found that they were opening the doors to a completely new world. The small-scale stewings and fusions of the old workers were transformed and greatly expanded into the carefully controlled activities of tremendous industry which is of vital importance to every minute of the existence of almost everyone in the modern world. Measured by any criterion you may choose: workers employed, value of products, numbers of new products, sociological effects, the expansion has been almost explosive.

This prodigious growth has brought its troubles to those who wish to acquire knowledge of the most important phases of chemical industry. Particularly within the last generation the field has become so immense that those associated with it tend to "learn more and more about less and less." Yet every alert person often has need for sources of information which will give a broad overview of a large realm and at the same time indicate sources of specialized information which may be consulted for greater detail. This book is intended for those who wish to obtain a significant survey of chemical industry as a whole, and of particularly important parts of it. Such an audience should include technical men and executives as well as students.

"Chemical Industry" covers a field which is so broad that it defies rigid classification. For the most part it deals with those activities where material is altered by means of chemical reactions. Yet the production of salt, or sugar, or of straight-run gasoline, involves only physical, not strictly chemical, changes. But such production is accepted to be a part of chemical industry. Though the limits of the study are somewhat indefinite there should be some sort of common framework, or skeleton, around which the subject matter can be presented. This framework can most easily be presented in the form of four questions: (1) What are the raw materials? (2) What is done with them? (3) What are the products and for what are they used?

(4) What are the important features of the economic pattern which weave the varied techniques into a workable industry?

The commonest and probably the most acceptable method of presenting the study of Industrial Chemistry is to discuss the answers to the above four questions for each of the various important divisions of the industry, based on the products. The bulk of this book is devoted to this type of presentation, but there are some items common to the industry as a whole which should be discussed first.

It would be pointless and confusing to go into the details of all the raw materials of all chemical industry in one place, but it is well to bring out the idea that almost everything on earth is, or may be, grist for the chemical mill. Rubber from the East Indies, sulfur from Louisiana, copper from Chile, salt from New York State, limestone from numerous quarries, bromine from the sea at any convenient location, nitrogen from the air around us, petroleum and coal from the ground beneath us; these and hundreds of similar items are the raw materials. The list indicates that the industry is, or can be, universal in its geography; almost universal in its utility.

Although each one of the chemical industries has certain economic minutiae which are peculiar to itself, there is a broad economic background which is common to the industry as a whole. Hence the first chapter of the book is on the economic pattern.

The scientific approach to the finding of the answer to the question of what is done with the raw materials has led to the formulation of the field of chemical engineering, which is organized around the physical unit operations and the chemical unit processes. These studies are more or less common to all the divisions of the industry, hence a section of the book is devoted to a brief explanation of the unit operations and unit processes, with a discussion of the equipment and materials for carrying them out.

Thus, the general background of the whole subject is hastily sketched in, in the first section. Then follows more or less detailed expositions of the more important divisions of the industry, based roughly on the types of products. No division or classification can be exact, for the subject is laden with interconnecting threads that cannot be separated and put into isolated cubicles. It will be noticed that the time-honored division into "Organic" and "Inorganic" categories has been broken down in several places, for the simple reason that rigid adherence to this fission of subject matter is not tenable.

A serious effort has been made to emphasize the unity of the whole industry by incorporating cross references which will direct the reader to other parts of the book for information presented in other fields which have bearing on the point under discussion. Numerous footnote references are given for original sources of information and classified bibliographies are incorporated at the ends of the chapters, which may serve as guides for the person who wishes to search particular fields for greater detail than is given here.

As the reader goes from one chapter to another, he will note striking differences in the exactness of the knowledge utilized in the different divisions of the industry. This is inevitable in a growing and complicated field. Some processes work with an exactness equal to that of a physicist's potentiometer, while others still go by rule-of-thumb empiricism, because the various branches of science have not given quantitative explanations for the phenomena involved. This only serves to emphasize that it is a developing field. Though progress has been tremendous, there are still large areas where exact knowledge has hardly come upon the scene. It is hoped that future editions of this manual will be able to report a steady march of exact science in all of the fields.

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BACKGROUND OF THE CHEMICAL INDUSTRY

Certain specific bodies of information, types of equipment and materials constitute the working tools of the chemical engineer. Every industry is based on economic considerations so the *Economic Pattern* is treated first. Next, the specialized engineering knowledge which is most applicable to the industry is discussed; along with the most essential pieces of equipment and instruments. A chapter on water is included in this section for it is an almost universal processing material.

INDUSTRIAL CHEMISTRY

CHAPTER 1

THE ECONOMIC PATTERN

Williams Haynes
Consulting Chemical Economist, Author of "Chemical Economics,"
Stonington, Conn.

To change the form of materials in order to increase their utility is the essence of all manufacturing; and to this end, from earliest times, man has employed both chemical and mechanical means. A beech tree is felled, sawed into lumber, and fabricated into a table. The waste wood, smaller branches and slabs, are thrust into a retort and by destructive distillation converted into methanol and acetone, wood tar and charcoal. In both cases the object is to produce more useful, more valuable goods; but there are obviously great, fundamental differences between a mechanical and a chemical treatment of the identical raw material.

Fire and the wheel—two early, exceedingly important discoveries of our primitive forefathers—stand today as symbols of these two great branches of industry. But it was only a hundred years ago that power was first seriously applied to tools and that the principles which underlie chemical reactions began to be intelligently comprehended. Prior to that time mechanical operations were handicraft; chemical processes were rule-of-thumb performances, discovered by accident, perfected by experience, and quite incomprehensible to the craftsmen who employed them.

With better chemical understanding, the employment of chemicals in industry has progressed from their use as reagents to modify the character of materials (as in primitive dyeing and tanning) to time-savers and cost-cutters (as when chemical bleaching supplanted sun bleaching and caustic soda replaced wood ashes in soap making), and quite recently to suppliers of many synthetic raw materials: colors and flavors, fibres and plastics, rubber and leather substitutes, etc.

Inevitably the pattern of chemical making and selling has been woven of certain unique economic elements. These are notably dissimilar to the economic processes of production and distribution in the mechanical industries.[1] They are, moreover, of prime consideration in the fair appraisal of any chemical project, the commercial operation of any chemical process, the profitable sale of any chemical product, and the successful management of any chemical enterprise.

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[1] Bass, L. W., Ind. and Eng. Chem., 37, 7, 409 (1930).

Therefore, for chemist, engineer, or businessman, a clear understanding of the chemical pattern is the beginning of wisdom.

CHEMICAL PRODUCTION

The chemical industry produces its wares by means of chemical reactions. As in the simple example of the beechwood subjected to destructive distillation, so always in chemical operations, each step produces a product which is an entirely new, distinct chemical entity and usually along with it one or more by-products which are also quite different from the raw materials and the main product.

This is, of course, the salient characteristic of all chemical manufacturing. It sets it apart distinctly from industries that grind and mix, weld and weave, cut and fashion, mold and polish their raw materials by all sorts of purely physical means. It is this characteristic that sets up the unique and distinctive economic pattern of all the chemical industries.

Unique Factors in Chemical Manufacture—Inherent in the chemical changes wrought in manufacturing processes are certain factors that vitally affect costs and competition:

1. Variation in yields.
2. Alternate raw materials and/or processes.
3. Disposition of wastes and by-products.
4. Interproduct competition.

Varying Yields—The tailor must cut his suit according to his cloth. This old proverb holds good generally throughout the mechanical industries. So many boardfeet of lumber, so many tables; so much sheet tin, so many quart cans; from a ton of rubber compound, this number of 6.50, 4 ply automobile tires. Broadly speaking, all fabricating manufacturers start even. This is not literally so, since there are always differences in manufacturing skill, in financial resources, and purchasing ability. Nevertheless variations in the cost of raw materials, against the output of finished wares of equal quantity and quality, are inconspicuous compared with what commonly obtains in chemical operations.

The classical anecdote of the broken thermometer which by unwittingly introducing a mercury catalyst so increased the yield of synthetic indigo that the whole process became commercially possible, vivifies the familiar fact that a minute difference in operating technique may have an enormous effect upon results. Small differences in the quality of raw materials, a little more or less pressure, a few degrees' difference in temperature or a few minutes in time, a slight change in the proportion of materials, or in the sequence of reactions, or of the form or hook-up of apparatus, may radically revise the chemical efficiencies of a process. Variation in yield is quite as integral a part of the chemical manufacturing operations as uniformity of size and shape is of the belt-line assembly of interchangeable parts.

Obviously variations in yield mean disparity of cost. Accordingly, at the very base of the chemical industry; that is, in its costs of production, an unstable factor is introduced that tips the balance heavily in favor of the more efficient producer. This unevenness at the foundation of competition is further heightened by the fact that the same chemical is often made from different raw materials or by different processes. Furthermore, many important chemicals which are main products in one plant may be produced as by-products in another operation.

Alternate Raw Materials—Vanillin, for example, may be extracted from the natural bean or it may be synthesized (1) from eugenol, an isolate of oil of cloves; (2) from guaiacol fractionated from phenol; (3) from iso-saffrol obtained from camphor oil; (4) from lignin recovered as a waste from the paper-pulp industry. For years the first two processes of synthesis have competed commercially. More recently the process employing wood-pulp by-product has reduced the price of vanillin from $3.75 to $2.00 a pound and promises eventually to supplant the older methods.

Sulfuric acid made as a major product by the chemical manufacturer must habitually compete, not only with surplus acid made in excess of their own requirements by superphosphate producers, but also with by-product acid from zinc and lead smelters.

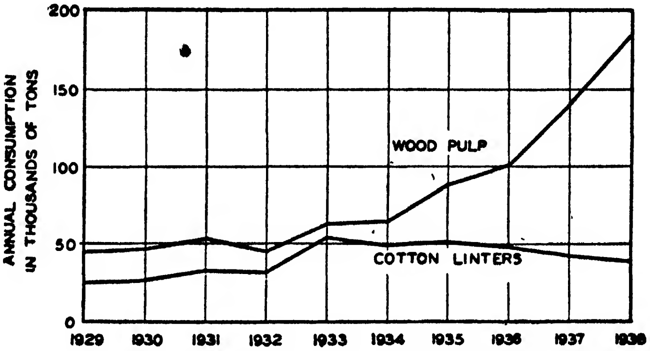

FIG. 1. U. S. Consumption of Wood Pulp and Cotton Linters in Rayon Manufacture. (Bureau of Agricultural Economics)

The competition between alternate raw materials is illustrated in Figure 1, which gives the annual consumption of cotton linters and of wood pulp by the rayon industry. The preferred material is cotton linters, as far as quality and low cost of conversion are concerned, but the cost of cotton has been maintained at an artificially high level by various agricultural aid programs and linters have been largely supplanted by the less expensive wood pulp.

Optional Processes—A good example of competing chemical processes is the manufacture of caustic soda by the lime-soda and the electrolytic operations. Here sodium chloride, the identical raw material, produces one of the most standard and widely used of all the industrial chemicals, caustic soda, but with a completely different group of accessory products. Using the lime-soda process a maker of caustic soda produces also soda ash, soda bicarbonate, calcium chloride, ammonium chloride, whiting, and carbon dioxide. His competitor employing the electrolytic process must dispose of chlorine and hydrogen. (For a description of these processes see Chapter 10, Alkali and Chlorine Production, and Chapter 11, Chlorine Products.)

Since the early thirties the controlling factor in this exceedingly complex competitive situation has been an astonishing growth of the consumption of chlorine. This growth has been consistently greater than the increase in the use of caustic soda. Accordingly, a premium has been placed on electrolytic production as against the lime-soda process and also upon the production of chlorine from any process that does not simultaneously produce caustic. The three big alkali manufacturers whose operations have long been traditionally associated with the lime-soda process—Solvay, Michigan, and Columbia—have all of late years erected electrolytic plants. Coincidentally more and more chlorine has been produced along with the manufacture of caustic potash and metallic sodium and by the process, operated at Hopewell by Allied Chemical and Dye, in which salt and nitric acid react to yield sodium nitrate and chlorine.

During the twelve years from 1925 to 1937 the sales of chlorine (omitting the substantial quantities produced for their own use by paper mills and chemical makers) increased from 38 to 286 thousand tons, valued respectively at $2,778,000 and $10,417,000.[2] This up-swing in chlorine consumption is naturally reflected in gains in the electrolytic production of caustic soda, which have been estimated by *Chemical & Metallurgical Engineering* as follows:

U. S. Production of Caustic Soda (Estimated)[3]

	1925	*1937*
By lime soda process	355,783 tons	488,807 tons
By electrolytic process	141,478 "	472,784 "
Total	497,261 "	961,591 "

Although authoritative current figures of alkali output are never available, the country's production of caustic soda now exceeds a million and a half tons, over fifty per cent of which has come from electrolytic plants since 1938 and with the normal growth being supplied practically entirely by this type of operation.

The trend of this interprocess competition is shown in Figure 2. Note that the price of chlorine has decreased as sharply as its production has risen, while the price of caustic soda remained essentially constant.

These impressive figures do not reveal all the vicissitudes of alkali marketing. The electrolytic process produces roughly a pound and quarter of caustic soda for every pound of chlorine. Accordingly as chlorine demand becomes more insistent, caustic soda output willy-nilly threatens to exceed requirements.

Several times during the depression years of the thirties the unbalanced supply of these joint products became dangerously acute. Caustic soda, formerly considered the main product, became the by-product. It was a novel and disconcerting experience to have the chlorine tail thus wagging the alkali dog. This competitive situation was adjusted, as we find when we consider the peculiar effects of chemical supply and demand upon chemical marketing policies, thanks chiefly to the increased requirements for caustic soda from the rayon and chemical industries. At this point it is only necessary to note that alternate processes, as well as alternate raw materials, introduce variations in costs of chemical production that disturb the equilibrium of chemical competition.

The example of the lime-soda and electrolytic processes also brings to the

[2] U. S. Census of Manufacturers, 1925, 1937.
[3] Chem. and Met., *46*, 2, 108 (1939).

front the two remaining factors inherent in chemical manufacturing which by causing variations in costs increases the pressure of competition; namely, by-product and inter-product competition. While the products associated with the production of alkalies by these two processes are not strictly speaking waste products, they are all of them obligatory by-products, produced regardless of demand. A considerable part of the increased demand for chlorine has been for use as a bleaching agent, a use for which it has almost completely supplanted calcium hypochlorite.

Wastes and By-Products—It is the consensus of good chemical engineering opinion that any by-product for which there is no market at a profitable price, or which may not be economically converted into a marketable product, should be disposed of as easily and cheaply as possible. To store it for posterity, whose chemical wants we cannot forecast, is not an intelligent procedure. To sell it or to convert it into a salable material at a loss is preeminently bad business judgment.

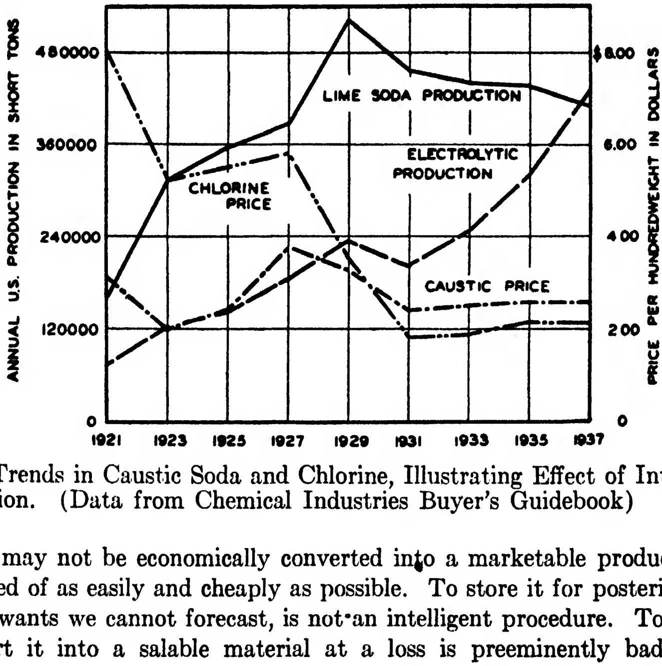

Fig. 2. Trends in Caustic Soda and Chlorine, Illustrating Effect of Interprocess Competition. (Data from Chemical Industries Buyer's Guidebook)

On occasion, however, the law overrides all economic considerations and demands that a chemical maker solve his waste problems less simply than by dumping onto a fill or pouring into a stream. Such compulsory operations were dubbed by John Teeple[4] "progress by injunction." He admitted that they often inspire fine technical ingenuity and require extraordinary sales ability, but he was one of the first to insist that waste is waste and not a holy fetish, the excuse for a research crusade.

A marketable by-product is in quite a different category. In fact, by-products that show profits loom large in the practical economics of chemical production. They often determine the commercial practicability of a process. Frequently they make all the difference between black and red figures on the final balance sheet of a chemical company. They are constantly sought and must be continually watched since the shifting of chemical demand, as in the case of caustic

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[4] Teeple, J. E., Ind. and Eng. Chem., *18,* 11, 1187 (1926).

soda and chlorine, may transform them into the main products. These by-products are always the foremost problem of fair cost finding in any chemical operation, and as such they are thrust into the front line in the competitive battle.

Severity of Inter-Product Competition—Although inter-product competition is not a unique characteristic of chemical manufacturing, nevertheless, like variations in yield, it is a more conspicuous and weighty factor here than in the mechanical industries. The replacement of bleaching powder by chlorine shows how complete are the victories won by chemicals in competition with each other. New coal-tar dyes and medicines can make older types as obsolete as Tyrian purple or powdered dragon's teeth. No pump or valve is replaced with the dazzling rapidity with which improved solvents and rubber accelerators succeed each other. Keen competition does exist between the different metals and alloys; but all this has been much intensified of late by the introduction of synthetic products of chemical manufacture.[5]

Furthermore, the owners of a textile mill or a machine shop may be quite confident that no revolutionary new process will force them almost overnight to scrap their equipment. They may be weaving rayon and knitting nylon where formerly they handled cotton and silk. They may be making castings of zinc that were formerly made of pig iron, and cutting tools from a chrome-manganese-iron alloy rather than of steel. But however much the materials and the styles may change, both know that the fundamentals of weaving and knitting, of casting and grinding, will persist.

The chemical maker, on the other hand, has no such comfortable assurance of stability in his basic operations. Different raw materials, a new set of reactions to reach the same chemical end, an improved set of apparatus—any of these may render his most important, most profitable process as obsolete as the Le Blanc method of manufacturing alkalies or the rectifying of vinegar to obtain acetic acid. New products and improved processes seldom arrive on the industrial scene without due warning and their introduction commonly takes time sufficient for competitive adjustment; nevertheless, in the chemical field this double-headed progress, in processes as well as in products, is very active.

High Obsolescence and Depreciation—Since chemical progress may come either in the form of new processes or new products, obsolescence of chemical plants is extraordinarily rapid. In fields where technical developments crowd thick and fast, it is quite possible that a new plant will be out-of-date before it can be built and put into production. This has actually happened in recent years in the equipment of operations to produce synthetic ammonia, synthetic methanol, synthetic rubber, plastics, and petroleum solvents.

The tendencies of modern chemical engineering practice have been towards bigger apparatus, higher pressures and temperatures, more exact control, so the mounting investment in equipment has weighted the costs of this obsolescence heavily. More than this, while there has been great improvement in corrosion resistant materials, chemical operations always involve abnormally high depreciation.[6]

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[5] Haynes, Williams, "Chemistry's Contribution: The Economics of New Materials," Princeton Univ. Press, 1936.

[6] "Depreciation Rates for Process Equipment," Chem. and Met., *45,* 80 (1938).

Large Scale Operations—Offsetting both these abnormally high capital charges are the efficiencies and economics of large scale operations made possible by the great volume of our chemical consumption. Mass production is an American industrial phenomenon. In the mechanical industries it has created the distinctively American technique of interchangeable parts and the moving assembly-line.[7] In the chemical industries it finds expression in the continuous, automatic process. It is common knowledge what the assembly-line has meant in the automotive, the airplane, and the firearms industries; but the increased output and decreased unit cost accomplished are not so great as the economics have made possible in chemical operations by the continuous, automatic process. The late Herbert H. Dow, himself one of our earliest and most successful practitioners of such large scale chemical operations, has summarized the economics effected.[8]

> In a product made on any ordinary machine tool it is necessary to increase the number of tools in proportion to the output, then to increase the number of operators in proportion to the number of tools employed. In chemical manufacturing many of the steps involved are capable of being handled in enormously larger units than is now customary without any increased cost of plant per unit of output and with no increase in labor costs, irrespective of the amount turned out. This is a great advantage that a chemical process has over a mechanical one, and it applies to containers, mixers, fractionating columns, vacuum pans, gravity types of filters, and to practically every continuous process.
>
> The most conspicuous methods of lowering costs in a chemical plant are: (1) larger equipment, to cut down the expense of chemical control and operating labor per unit of product; (2) automatic analysis, to save the labor expense of chemists making routine analytical tests at regular intervals and to secure results more quickly and more certainly, with the chance of error due to the personal factor reduced; (3) automatic operation of the equipment, which is governed by the automatic analyzer, all leading to the final *desideratum*; (4) a continuous process which is both automatically controlled and operated.
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> There are, of course, other means for labor saving, such as motion study, the co-ordination of supplies, and other means for increasing the effectiveness of the human element. Such measures are of relatively less importance in operating large sized chemical equipment than in the case of machine processes.

Unit Processes and Operations—In the commercial development of the continuous process operated on a large scale and under automatic control, the concept of the unit operation and the unit process has been exceedingly valuable. In welding together a series of disjointed batch operations into a combined series, in which the raw materials are introduced at one end and the finished products—main product and by-product—are withdrawn at the other, the clearer understanding of each step was essential, and paradoxically by studying these different units individually their combination in many sequences has been simplified. The more important unit operations of chemical technique are: (For a summary of the various unit operations, see Chapter 2.)

Heat transfer
Fluid flow
Crushing and grinding
Mixing
Mechanical separation
Distillation
Evaporation
Crystallization
Filtration
Absorption
Drying

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[7] Roe, Joseph W., "Interchangeable Manufacture," Trans. Newcomen Soc., *17*, 165 (1936-37).

[8] Dow, H. H., Ind. and Eng. Chem., *22*, 113 (1930).

These, it is immediately noted, are all physical operations, presenting engineering problems, while the processes grouping the chief chemical reactions are as follows: (For a summary of the various unit processes, see Chapter 3.)

Oxidation
Reduction
Nitration
Sulfonation
Hydrogenation
Esterification
Amination
Acetylation
Diazotization
The Friedel-Crafts reaction
Halogenation
Hydrogenolysis
Hydrolysis
Hydration
Alkylation
Cracking
Polymerization
Depolymerization
Resinification

Most of these processes are obviously applicable only to organic technique and it has been in organic synthesis that the unit concept has proved most valuable. Commercial production of many organic compounds—a dye manufacturer will make scores of colors often in comparatively small quantities—necessitates a juggling of apparatus and equipment in different series of operations and the handling of different materials for reaction. Yields are of prime importance and the intensified research on the unit operations has been very fruitful in studying analogous phases of various reactions, making possible careful comparisons of slight variations in operating technique.

The competitive advantage of being the low cost producer among a group of chemical makers is so obvious and so great, that since the conditions of chemical production create exceptional opportunities in this respect, every firm strives continually to achieve this enviable position. What is familiarly known throughout the industry as "know how"—an intimate knowledge of the little technical tricks of chemical-making, gained by operating experience and capitalized by alert ingenuity—is highly prized, and research to save time and power and to increase yields and quality, is as standard practice as double entry bookkeeping. Research is recognized as a prime necessity in any chemical enterprise, and the industry pays the biggest research bill in the country in hard-headed appreciation of the fact that only constant research can assure the profits of today and insure the sales of tomorrow.

THE ROLE OF RESEARCH

Types of Research—In the chemical industry there is no question, as Tyler[9] has pointed out, whether research shall be done or how it shall be done, but what lines of research shall be followed up; and he has itemized the various types of research as follows:

1. *New Uses for Present Products*—For example, an organization making synthetic ammonia, primarily for conversion to nitric acid and other chemical plant use, found that ammonia was an excellent antichlor for water purification.

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[9] Tyler, Chapin, "Chemical Engineering Economics," pp. 22-23, McGraw-Hill N. Y., 1938.

2. *New Products from Present Materials and Techniques*—For example, an organization making synthetic ammonia and by-product carbon dioxide developed processes for making ammonium carbonates and urea from these materials. Furthermore, the technique by which synthetic ammonia was made was applied in synthesizing such alcohols as methanol, normal propanol, and isobutanol.
3. *Demands for a Specific Product or Service*—For example, a manufacturer of mechanical household refrigerators desired a refrigerant that was nontoxic, nonflammable, and that could be used at reasonably low pressures. In response to that demand, the dichloro-difluoro-methane type of compounds was developed.
4. *Latent or Generally Unrecognized Needs*—For example, the public did not demand air conditioning until air conditioning was available. The latent demand, however, was perceived by engineers and was finally exploited on a large scale.
5. *Suggestions, Ideas, and Inventions Originating Outside the Organization*—Thus, a company desiring to enter a field of manufacture might do so by acquiring rights to use processes developed outside the company. The company would then be enabled to begin commercial operations with relatively little delay and could at the same time establish a research program.
6. *Savings through Improvement of Present Products and Processes*—For example, the sulphuric acid industry in the United States is about 150 years old. Yet, improvements in process continue to be developed.
7. *Development of Radically New Techniques*—Much cheaper strong sulphuric acid was made possible when the contact process was developed. Previously, the strong acid was made by concentrating the relatively weak chamber acid.
8. *Development of New Raw Materials*—As long as nitric acid was made from nitrate of soda and sulphuric acid, the cost depended not only on the cost of the two raw materials, but upon the credit from by-product niter cake. One could not reliably forecast the cost of nitric acid. When the ammonia oxidation technique was developed, the economic position of nitric acid was entirely changed. Neither nitrate of soda, sulphuric acid, nor niter cake entered into the new process. Only the cost of ammonia need be considered, and this has proved to be a relatively low and gradually declining cost.
9. *Fundamental Research*—Research undertaken with no immediate practical objective may be termed "fundamental research." Thus, a company engaged in manufacturing derivatives of cellulose might study the structure of cellulose. The objectives of such a study would be purely theoretical. Years might elapse before the attainment of any significant results. Should the research be undertaken in order to discover new derivatives of cellulose, with the hope that these might exhibit useful properties in relation to the company's existing business, then there would be a practical objective. Such research may be termed "pioneering applied research." Thus, the distinction between fundamental research and pioneering applied research is based principally upon the scope of the work and the extent to which it is limited by recognized practical objectives.

The word "research," like "synthetic," has been stretched by careless use far beyond its literal meaning, and one hesitates to confound the confusion; but the three purposes for which development work is undertaken may be further clarified by a paraphrase.

"Search" is the hunt for new products, new applications, and new processes.

"Re-search" is the study of existing products or processes to lower their costs or increase their value.

"Pre-search" is the exploration for new scientific data of immediate fundamental importance and possibly of ultimate commercial application.

Such a classification purposely emphasizes the ends of research, and properly so, for the success of any research program depends not a little upon sharply focusing its objectives and then keeping the eye fixed on the goal.[10] For research has ceased to be an individualistic effort, and in team play the spirit and cooperation of the group is best concentrated upon a simple direct, common end. For tangible results, work upon existing products and processes shows the most

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[10] Stine, C. A. M., Ind. and Eng. Chem., *24*, 191 (1932).

immediate returns, and including as it does, the "service" rendered customers and all testing work, it undoubtedly embraces a goodly majority of the research projects in the chemical field. At the other extreme is research in pure science.

Plant Development—Whatever type of research is carried on, funds must be available to carry it forward. Financially speaking the investment in research must be capitalized; and this requires a further, greater investment in commercial scale development, in plant capacity, in the packing and shipping departments, and finally in sales work. Interdependent relationships exist between the growth of research, the growth of manufacture, and the growth of sales which, if the research organization functions soundly, demands foresighted planning and carefully coordinated expenditures.

Correlation of Research and Expansion—These correlated relationships have been expressed in ratios that are exceedingly illuminating. Based upon a comparative study of the published balance sheets of representative chemical manufacturing corporations Gaston duBois, vice-president, in charge of Monsanto's research and development, reports[11] that—

"We have found that in the chemical industry the turnover in a year is about equal to the plant capital investment, and at the present time research expenditures in the case of some of the progressive concerns amounts to about 3⅓ per cent of the yearly gross sales. If we assume an increase in business of 15 per cent yearly, it follows that the plant capital investment will have to increase in about the same proportions, and if we assume a 15 per cent return on the capital invested, then the cost of research will amount to about 22 per cent of the profits.

"The table which I have here indicates that under such conditions business will double in five years and treble in eight years and quadruple in ten years, and during this period research expense would increase from $1,000,000 to $4,000,000. At the end of this period about $25,000,000 new capital will be required per year to carry on at this rate. If the figures which I am presenting mean anything, they do indicate what an important bearing our research policies will have on finance, on manpower for manufacture, on the need for proper organization to meet increase in business, inasmuch as the employments of 15,000 men in 10 years to take care of the business shown on this chart is a "major operation." (See Table 1.)

Superficially regarded this table is in one respect misleading. While it undoubtedly holds good for the financial requirements of an established and efficient organization, it obscures the time lapse that must be bridged between laboratory research and plant production. It is a sort of chemical axiom that six years elapse between the date of discovery and that of the first commercial shipment. Certainly the chemical made in the test tube is far from the commodity shipped in the tank car.

In a few extreme cases it has been impossible to translate a laboratory process into a large scale plant operation. Almost always the commercial realization of the experimental product or process involves more time, effort, and expense than at the outset seemed called for, and attempts to short cut this development work usually prove false economy.[12]

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[11] Gaston duBois, "The Financial Aspects of Research," address, St. Louis, May 14, 1937.

[12] Lesher, C. E., and Archer, A. A., Chem. and Met., *46*, 343 (1939).

When Herman Frasch was developing his revolutionary process for melting sulfur underground and pumping it to the surface, he was perforce compelled to jump from paper calculations to the field operation. His test tube was a drilled hole ten inches in diameter and five hundred feet deep.[13] At his desk he had worked out his temperatures and pressures, thermal efficiencies and specific gravities. In no way could he check these experimentally. No model, or semi-commercial plant could be erected for intermediate testing. Ordinarily, however, the laboratory experiment is carried forward to plant production through these several steps:

TABLE 1

MILLIONS OF $ CAPITAL INVESTMENT

Year	*Plant Equipment*	*Working Capital 20 Per Cent of*	*Sales*	*Profits 15 Per Cent*
1	30.	6.	30.	4.5
2	34.5	6.9	34.5	5.17
3	39.67	7.94	39.67	5.95
4	45.62	9.12	45.62	6.84
5	52.46	10.49	52.46	7.87
6	60.33	12.07	60.33	9.05
7	69.38	13.88	69.38	10.41
8	79.79	15.96	70.70	11.97
9	91.76	18.35	91.76	13.76
10	105.52	21.10	105.52	15.83
11	121.35	24.27	121.35	18.20

MILLIONS OF $ NEW CAPITAL

Year	*Research Expense 3⅓ Per Cent of Sales*	*Plant Equipment 15 Per Cent Increase*	*Working Capital 20 Per Cent of*	*New Money Required*
1	1	4.5	0.9	6.4
2	1.15	5.17	1.04	7.36
3	1.32	5.95	1.18	8.45
4	1.51	6.84	1.37	9.72
5	1.75	7.87	1.57	11.19
6	2.01	9.05	1.81	12.87
7	2.31	10.41	2.08	14.80
8	2.66	11.97	2.39	17.02
9	3.06	13.76	2.75	19.57
10	3.52	15.83	3.17	22.52
11	4.04	18.20	3.64	25.88

1. *Test tube or beaker*—during which stage the chemistry of the process is thoroughly explored and its basic technical principles tested. At this point too, the "novelty" of the idea should be examined in the patents and literature and its commercial possibilities checked over for cost and supply of its raw materials and price and demand of its market. In other words, at the earliest moment and least expense determine whether or not here is an idea worth developing.

2. *Small model*—commonly of glass, but large enough to allow the use of ordinary commercial raw materials and to permit the manufacture of sufficient quantities of finished product for tests as to quality. This model should be kept

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[13] Frasch, Herman, Chem. and Met., *10,* 78 (1912).

flexible as its chief purpose is to study all the operating variables in design and materials in order to discover optimum working conditions.

3. *Large model*—often embodying apparatus made of the special engineering materials expected to be employed, and designed to determine the efficiency of the process in plant operation. This is the critical step in ascertaining whether the laboratory idea can be brought to the plant, and the large-size model should still be kept flexible and the tests should be run for many consecutive days.

4. *Semi-commercial unit*—best kept as small as practical, but sufficiently large to be handled by ordinary plant labor and to produce enough finished goods for testing thoroughly in all its important commercial uses. At this stage the objects are to determine the design, materials, and hook-up of the various apparatus and equipment; the plant-scale capacities and requirements and the capital investment necessary in this plant upon a full commercial scale; the costs of labor, power, and materials involved in plant production.[14]

Brought with scrupulous care through these testing stages the chemical and engineering soundness of the project should have been established beyond doubt. At the same time the economic risks should have been appraised and discounted since the conditions peculiar to chemical production intensify competition through disparity of costs. It has been said that nobody should undertake to make a chemical unless assured that his costs will be at least 30 per cent below those of the most efficient producer in the field because he will need that leeway to gain a foothold in an established market. In the first place his competitor's costs are probably 10 per cent lower than he suspects. His competitor will cut the price 10 per cent to keep him out. He will have to sell 10 per cent below established suppliers in order to win customers. A good deal more sober truth is buried in this jocular warning than appears on the surface.

The most important factors distinctive of chemical manufacturing are those that cause the disparity of costs. When one producer enjoys the advantage of lower costs than his competitors he has open to him three courses of sales policy. He can (1) sell at the same price and reap extra profits; he can (2) cut the price to a point which still shows him a basic profit but which is much less profitable, if not actually unprofitable, to his competitors; or he can (3) set a price below his competitors' cost and though drastically curtailing his own profits, he can, if it seems expedient, maintain such ruinous competition for a long time.

Rapid Technical Advances—All elements peculiar to chemical production —varying yields, optional raw materials and processes, the disposal of by-products, progress both in products and in processes—condition the chemical industry to a high, swift tempo. They intensify competition. They create excessively high rates both of depreciation and obsolescence. They subject any chemical-making enterprise to exceptional economic risks. They demand of management a clear mind, wide open to progress, backed by financial resources amply able to sustain elaborate research programs, to scrap outmoded products or obsolete plant, to undertake new ventures both in manufacturing and in selling.[15]

The conditions governing chemical production are certainly onerous, but they are also stimulating. The philosophy of the industry accepts change as a

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[14] Elgin, J. C., Chem. Industries, *24*, 313 (1934).

[15] Morgan, D. P., Jr., The Chemist, March, 1932, 170-202.

part of progress, and the stubborn inertia which resists any innovation that so frequently characterizes older industries, is replaced by an adventurous initiative that actively seeks out new things. The energy displayed in installing new processes and the courage in marketing new products, are both undoubtedly supported by the rather favorable conditions that surround chemical distribution. For, if the chemical manufacturer must face distinctly difficult conditions in production, compared to many other industrialists he enjoys advantageous marketing conditions.

CHEMICAL DISTRIBUTION

First, the demand for chemicals is notably stable. This stability is grounded upon both multiplicity of products and diversity of demand. Although the demand for individual chemicals often varies greatly, the whole chemical market rests upon foundations that are at once broad and deep, and correspondingly solid.

Most chemical companies make and sell a wide variety of diverse products. The numerous chemical consolidations and mergers which marked the booming decade of the twenties were commonly inspired by a desire to broaden the base of operations. Throughout the depressed thirties intensified research brought to the market an astonishing number of new—many of them very important—products. Accordingly, most companies manufacturing the basic chemicals sell a long list of well diversified items, the majority of which are consumed in a wide variety of industries. Thus the curves of seasonal demand and the more serious dips of our periodic periods of depression are flattened out.

This stability of demand is further increased by the rôle that industrial chemicals play in our modern economy. Beginning about 1910, with the commercial introduction of synthetic fibres and plastics, a great expansion in the consumption of chemicals has sprung from the growing use of chemical substitutes for natural raw materials. During the last century American chemical consumption had increased almost in proportion to the increase in the value of all American manufactured wares. Our growing output of glass, soap, paints, cloth, paper, leather, rubber, steel, and alloys increased our consumption of chemicals. (For details of the chemicals and processes employed in these fields see respectively Chapters—glass, 20; soap, 42; paints, 25 and 26; paper, 37; leather, 45; rubber, 39; steel, 23.) This development was more rapid here than in any other country. Even prior to the First World War our total chemical production, measured in dollars or in tons, was substantially larger than that of either England or Germany. Most of our output was then of the so-called "heavy chemicals," chiefly inorganic acids and alkalies.

Synthetic Chemical Materials—Synthesis has enormously broadened the use of chemicals resulting in a corresponding increase in chemical production. Today our national chemical output is greater than the combined productions of England and Germany.

This market opened up slowly. The first rayon plant in the United States came into operation in 1910. Ten years later, from seven plants, the output was only a little over 8 million pounds. In another eight years (1928) it reached 100 million pounds. Five years later (1933, in the depth of the depression) the total reached 215 million pounds; four years later, 340 million pounds; in 1940, the volume passed the 500 million pound mark. See Figure 3.

The growth of the plastics and synthetic resin industry is recorded in a similar, steeply ascending curve, which has climbed from less than 5 million pounds in 1920 to above 200 million pounds in 1940. Substitute rubbers of various types, for which there are as yet no reliable statistics, promise after the comparatively slow increase of the initial years to expand their output greatly in the years before us.

To supply such chemically made materials has become a chief economic function of the American chemical industry, a main cause of its consistent growth, one of its principal sources of profit. Whenever one of these synthetics replaces a natural material, a double gain is scored for the industry. Not only does its production involve the consumption of vast quantities of chemicals, but it greatly increases the form value of these chemicals.

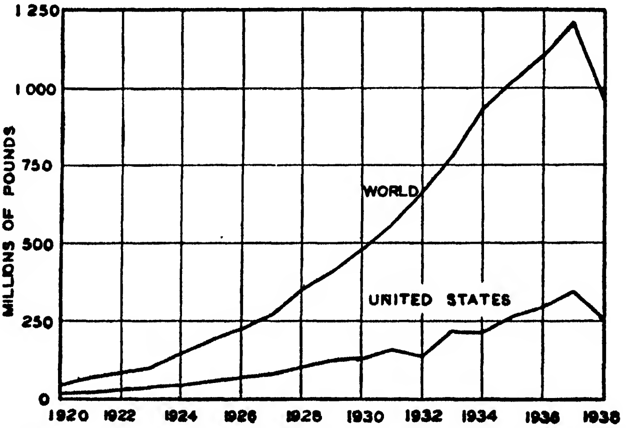

FIG. 3. United States and World Annual Rayon Production. [Textile World (1920-1929) and Rayon Organon (1930-1938)]

Move Toward the Ultimate Consumer—This has been recognized in financial circles and well expressed by a banker: "Growth throughout the depression has been due chiefly to the enormous increase in the production of rayon, plastics, lacquers, and similar chemical substitute materials."[16] It has also been recognized by the industry itself and has inspired the expansion of many companies from the strictly chemical making group out into the chemical converting groups. The du Pont Company has long been selling paints, lacquers, explosives, rayons, cellophane, even fabricated plastics. The interest of other large chemical corporations in similar lines is more recent, but exceedingly significant. The alliances of Monsanto with Fiberloid and Resinox, Union Carbide with Bakelite, American Cyanamid with Beetle; the internal development of their own plastic materials by Dow; and in the opposite direction, the manufacture of phenol by General Plastics, forecast that plastic materials are destined to be made by the companies which make the chemicals out of which these are formulated. Syn-

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[16] White, Bert H., Chem. Ind., *45*, 658 (1939).

thetic rubber displays the same tendency. Synthetic fibres might be reasonably expected to follow this same economic groove.

All these, and similar, synthetic raw materials bring the chemical manufacturer a long step closer to the ultimate consumer. Selling acids and alkalies, colors and solvents, in bulk to industrial purchasing agents to be employed in processing as chemical tools, is a vastly different merchandizing technique than persuading Mrs. John Doe to buy a dozen plastic cups for her picnic hamper. The sale of these synthetic materials is a stout bridge over this gulf. Frequently it is leading the chemical manufacturer straight to the consumer market.

Economic Function of Synthetics—While these synthetic materials are thus acquiring a new commercial significance in the chemical industry, their technical importance has long been appreciated. They began in a serious way in 1856 when Perkin's synthesis of the first aniline color blazed the way to the coal-tar dye industry. In this fertile field grew synthetic perfumes, synthetic flavors, synthetic medicinals. Here were garnered rich sheaves not only of applied organic chemistry, but also of practical chemical economics. It was early learned, for example, that these synthetic materials made six great contributions to modern industry:

1. Constant quality that tends continually to improve.
2. Stable price that tends continually to lower.
3. Unique chemical and physical properties, not made available for human use by any natural product.

These three direct contributions to modern industry are translated into better goods, cheaper goods for the benefit of all mankind. Another three are broader contributions to our economic system, often with political implications and frequently upsetting international trade, but in the long run, distinctly assisting general progress and universal well-being. For these synthetic materials are able to exert effective force in the following directions:

4. To control, or even to break, local natural monopolies, long skillfully exploited at the expense of the rest of the world; and conversely to enable nations lacking certain raw materials to manufacture substitutes for their own needs within their own boundaries.
5. To release land and labor, formerly devoted to producing industrial raw materials, for the purpose of growing foodstuffs.
6. To conserve the resources of certain exhaustible and irreplaceable natural raw materials by furnishing acceptable substitutes for their less vital uses.

Synthetic vs. Natural—In the battle between land and laboratory, the synthetic material always enjoys certain advantages over its natural rival. When first a new synthetic appears on the market it comes into direct competition with some existing material. It may be the chemical twin of its natural competitor, as indigotin and vanillin are identical with the active coloring and flavoring principles of the indigo plant and the vanilla bean. It may be an acceptable substitute, as Fabrikoid for leather in automobile upholstery or Thiokol for rubber in the gas station's delivery hose. It may be some unique chemical compound, unknown in nature, as glass, which is after all one of our oldest synthetic materials, or the sulfonated higher alcohols, one of our latest.

One notes too, that aside from these differences in composition, the adjective "synthetic" is applied to the products of quite distinct types of processes. There are synthetics like sulfapyridine and mercurochrome[17] made by building up complex organic molecules through an elaborate series of reactions, and those like so-called synthetic ammonia and synthetic methanol, made by some simpler process from chemical materials that replace more complicated chemical treatments of natural raw materials.

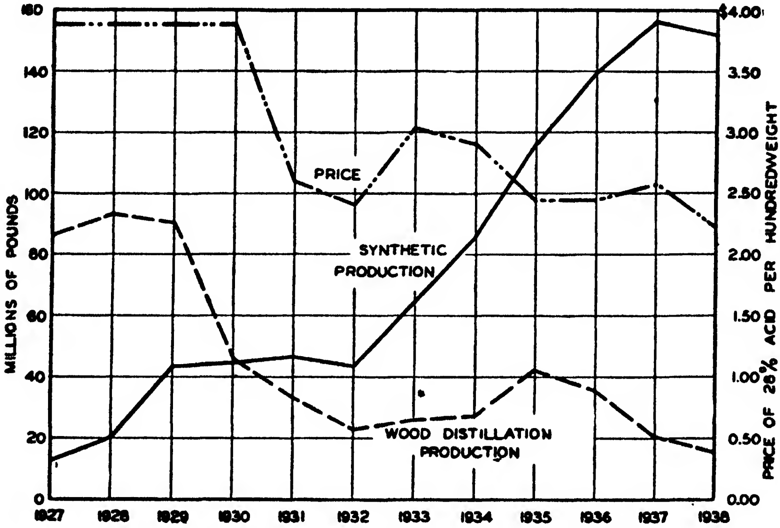

FIG. 4. Competition of Synthetic vs. Natural Materials. U. S. production and price of acetic acid. (Basis of 100 per cent acid.) (Production figures from U. S. Tariff Commission; prices from Chemical Industries Buyer's Guidebook)

The buyer of a new material has usually little curiosity about its formula, or how it is made, or from what it is made. He is critically interested, however, in what it can do and how much it costs. Any newcomer in the market must offer him some advantage of value. This is quite as true of a new supplier as of a new product. Accordingly, a new material is usually cheaper, though sometimes a higher quality, or some wanted characteristic, will offset a higher price.

The result of one battle of synthetic vs. natural materials is shown in Figure 4. Synthetic acetic acid has all but replaced the natural product in a little over one decade. During the same period, price has been reduced 40 per cent and average consumption has increased some 70 per cent.

Advantage of Better Value—When synthetic citric acid appeared on the American market in 1919 the price of the acid made from natural lime citrates was $1.10 a pound; a year later the price was 40¢, or actually 10¢ a pound less than in 1915 before the war inflation. On the other hand, in 1933, when the price

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[17] Respectively para-amino-benzenesulfonamide pyridine, $C_{11}H_{11}N_3O_2S$, and disodium 2.7 dibromo 4 hydroxy-mercurifluorescein, $C_{20}H_8O_6Br_2Na_2Hg\ 3H_2O$. For a description of the manufacture of these pharmaceuticals, see Chapter 34.

of rubber was 31¢ a pound, Neoprene was first offered at $1.05. Even this high price did not cover the actual cost of manufacture, to say nothing of the six years' research which the du Pont Company had invested in it. Despite price, Neoprene found a market because of its superior resistance to oils, benzene, gasoline, and alkalies. As output increased, costs were reduced, and the price was lowered to 75¢ a pound in 1937 and 60¢ in 1940. By this time more than two hundred and fifty customers, including practically all the rubber companies, were buying Neoprene for uses in which its peculiar properties were superior to rubber. Hundreds of similar experiences show that the material advantage of price invariably rests with the successful synthetic, and as the volume increases, the price of the chemically made material is successively reduced.

Causes of Fluctuating Costs—Because the supply of any manufactured commodity is under control and may be adjusted to meet changes in demand, its price can more easily be held stable. On the other hand, the price of any natural raw material is prey to many powerful influences over which the producers have little or no control. Drought or hurricane or insect infestation result in crop failures that run prices up. Excessive planting or extraordinarily favorable weather conditions bring in a bumper crop that depresses prices. Many important natural materials come to our American factories from the ends of the earth —gums from Australia and Arabia, oils from China and South Sea Islands, waxes from Mexico and West Africa, tin from Bolivia and the Straits Settlements, chrome from Turkey, Rhodesia, and the Philippines—and to the acts of God are added the deeds of men: wars, revolutions, fluctuations in currencies, speculative buying and selling.

The interplay of these economic forces upon prices is aptly illustrated by natural and synthetic vanillin. Chemically the two are identical, but the natural material is favored for its natural impurities which impart a superior "bouquet" to the flavor and "fix" that flavor more permanently. Natural vanilla is extracted from the beans of a vine that reaches maturity in three years and after eight years ceases to yield a profitable crop. Each season the vines must be cultivated and trimmed back, and young plants need to be continually brought along to replace the outworn stock. Vanilla is native to Mexico, which still produces the most favored beans; but its cultivation has spread to many parts of the semi-tropics, and the largest commercial center is the Island of Madagascar. Prices fluctuated widely. During the nineteen years prior to the end of the First World War, 1918, quotations of the Mexican beans in New York ranged from a low of $2.50 a pound (1914) to a high of $11 (1900) with an average close to $4, while the Bourbon (Madagascar) grade was quoted at a low of $1 a pound (1905-06) and a high of $4.75 (1901) with an average price of about $2.25.[18] Synthetic vanillin appeared on the market in 1876 at $80 a pound. This price was successively reduced till in 1924, substantially half a century later, it sold at $8, one tenth of the initial price. By 1938 it had been reduced to $2 a pound.

Prices in a Vicious Circle—Just at this time, 1924, a revolution in Mexico and bad weather in other growing centers, gave Madagascar planters a corner on supplies and they ran their price from $2.65 up to $9. Their perfectly human selfishness had two logical results. Planting of vines was stimulated in all growing centers. Substitution of vanillin for vanilla was promoted in all consuming

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[18] "Oil, Paint and Drug Reptr. Yearbook." 1918, p. 157.

fields. By 1927 the world crop of vanilla had nearly doubled. By 1932 the price had sunk to 50¢ which hardly paid to pick and cure the beans. Accordingly, plantations were neglected with the natural result that in 1934 another acute shortage arose, thus completing the vicious circle.

Meanwhile increased consumption of vanillin had enabled American manufacturers to reduce their price from $8 to $3, with the result that the 1934 famine price of Bourbon beans rose, not to $9, but to $3.20. Control of fluctuations in the price of natural vanilla had plainly become a function of the price of synthetic vanillin. It is notable, too, that despite these fluctuations the synthetic price has steadily declined. The end is not yet, for in 1937 the introduction of vanillin from wood-pulp waste brought the price down to $2.

In 1913 we imported 1,049,617 pounds of natural vanilla beans: twenty-five years later, 1938, 472,478 pounds.[19] During the same period our production of synthetic vanillin has grown from zero to 348,461 pounds, which represents chemically the equivalent in flavoring principle of over 139 million pounds of beans. In commercial practice about three parts of vanillin replace 500 parts of vanilla extract, so that for five parts of natural vanilla flavor we are using today about 3,000,000 parts of synthetic.[20] In industry the use of natural vanilla has virtually vanished and what little we import goes into extracts for household use in justification of the label "made of natural vanilla beans, fortified with vanillin." In this delicate matter of the taste of foodstuffs these amazing figures show how far we have come from the early prejudice that was raised by the mere mention of "synthetic." Twenty-five years ago rayon was introduced as "artificial silk" and the public regarded it a cheap and nasty substitute. In 1939 Nylon was offered as a new, unique synthetic fibre and within six months after the first Nylon hosiery was put on sale American women had bought 17 million pairs at a price above rayon goods but below the best silk, a record for "consumer acceptance." In industrial circles acceptance of new chemically made materials has progressed till they are sought out by progressive manufacturers and welcomed as opportunities not only to lower costs, but also to create new lines.

Advantage of Uniform Quality—It is said that no ice cream, soft drink, or candy maker, no bakery, no chewing tobacco or cigarette manufacturer—these are the chief industrial consumers of vanilla—ever makes the substitution of vanillin and comes back to the natural extract. None of them is able easily to readjust his retail price to offset fluctuations in the costs of raw materials. Therefore, a stable price, which means a stable manufacturing cost, is even more important than a low price.

Almost as advantageous is uniformity of quality. The flavor of vanilla beans grown in different localities differs so markedly that well identified grades are based on origin. Even at a given growing center, variations in weather conditions from season to season and the degree of care and skill exercised by different planters in cultivating, harvesting, and curing the crop, result in variations in quality. The use of the beans as flavoring agents becomes, therefore, an art that must be painstakingly practiced if uniform results in the finished product are to be maintained.

Against this, an ounce of vanillin invariably produces the identical flavoring

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[19] Statistical Abstract of the U. S.: figures of the Census Bureau.

[20] Merck's Index, 5th Edition, 1940; 460-61.

effect. Regardless of when or from whom it was bought, it is always the same so that once an industrial recipe is chosen, the result so far as a vanilla flavor is concerned, is constantly assured. Such standardization fits modern factory methods. Price stability and established quality suit all synthetic products to modern streamlined production.

Chemical Demand—The demands of industrial consumers are continually more exact. Greater precision in manufacturing methods and more discriminating requirements from their customers alike compel all manufacturers to select their materials with great care. Again, the man-made materials enjoy an advantage. They can be tailor-made to fit the specifications.

Modern textiles, for example, are woven of many combinations of natural fibres and different types of rayons. Thus special fabrics, fitted to particular uses from a bathing suit to a tire tread, are created. Modern coatings have become highly specialized to meet conditions of wear ranging from the wing tip of an airplane to the timbers in a mine.

Chemical Demand Is Always Changing—Chemical demand is not static, but dynamic, indeed prompted to change by man's fondness for novelty and under compulsion to change because of constant technological progress. Many of these changes are initiated far beyond the control of the chemical maker, but he is always stimulating them by his endless search for new products and his tireless efforts to win new markets. Often he promotes changes that get out of his control, as the expanded demand for chlorine which has not only pushed bleaching powder off the market, but also dislocated the supply of caustic soda.

Producers' Control over Consumption—Over the intensity of demand chemical producers have also little control. Chemicals are used as tools, or as materials, by other industries. Their consumption depends, therefore, upon the activity of those industries. Soap and rayon are big consumers of caustic soda; but the caustic producers can do little directly to increase the consumption of alkali in either goods. Their total sales depend upon the national sales of soap and rayon, upon the tons of paper being produced, the barrels of gasoline being refined, upon all sorts of goods which no sales effort of theirs can increase. The industrial buyer purchases chemicals "for his requirements," as so many chemical sales contracts read; and he can seldom be tempted to overload his inventory with stocks of standard chemicals.

This inflexibility of chemical demand and the inability of chemical makers directly to increase consumption, has baneful effects upon the price of any chemical the supply of which cannot be quickly adjusted to market conditions.

The control that price exercises over supply and demand has been so effectively obscured in our workaday world today that many are tempted to ignore it completely. But the maker of basic chemicals is not permitted long to forget these fundamental economic principles. The price of chemicals is more promptly and delicately responsive to these influences than are the prices of most other manufactured goods.

Control of Supply through Price—White arsenic, As_3O_2, is produced in the United States solely as a by-product recovered from the flue dust and flumes at lead and zinc smelters. Prior to 1915 the price, 3¢ a pound or less, did not make it profitable to install the necessary equipment, and out of a potential supply of some 15,000 tons, only one thousand was produced. At that time our normal demand of 10,000 tons—4000 in calcium and lead arsenates, 1500 in sheep dips, 1200 for weed killers, 2000 for plate glass, and 1000 for miscellaneous uses—was met by imports chiefly from Mexico, Japan, Spain, and Germany.

In 1916 war demands, coupled with the high cost and uncertainties of ocean transportation, raised the price to 8¢ a pound. Then our domestic smelters installed recovery plants or enlarged existing operations. The next year a big new demand appeared suddenly in our domestic market. The cotton boll weevil had become a menacing pest and calcium arsenate was found to be the most effective means of its control. So rapidly did this demand grow that in 1922-23 it far outran supply and the price of white arsenic soared to a peak of 18½¢. This high cost for the raw material resulted in a delivered price of calcium arsenate to southern planters of from 25 to 30¢, which combined with the low price of cotton and light weevil infestation reduced this new demand sharply. By the end of 1924, the price of white arsenic had declined to 6¼¢.

Since 1916 our domestic consumption of white arsenic has moved up from 10,000 to 35,000 tons, the insecticide industry alone consuming more than twice the total pre-war demand. Half the market is now supplied from domestic sources. Legislation has made it compulsory in most states to recover arsenic wastes, but the growth of the total demand has created a market that, despite the wide fluctuations of sales of insecticide arsenic, is nevertheless stabilized at a total requirement comfortably in excess of domestic output. This demand is large enough to absorb all domestic arsenic and the larger tonnage makes the old pre-war price of 3¢ profitable.

Demand for insecticide chemicals is always problematical. It is inevitably seasonal and generally unpredictable. A year of big insecticide sales, because of temporary triumph over the pest, is apt to be followed by a season of small demand. A consumption of 20 pounds of calcium arsenate to the acre of cotton land throughout the area of weevil attack is indicated by average standard practice in control. However, effective demand cannot be measured by the degree and extent of weevil infestation. The cotton planter is influenced in his arsenate purchases: first, by the cash surplus from the sale of last year's crop; and second, by the prospective price of the cotton in his fields. Furthermore, he waits till the actual time of application before buying so that a spell of weather either especially favorable or unfavorable to the insects will materially affect his purchases. In recent years the low price of cotton has sharply curtailed the use of calcium arsenate even to the extent that many planters favor "letting the weevils eat up the crop surplus."

So capital an authority as F. Y. Robertson has estimated the cotton field market for calcium arsenate at "approximately 5000 to 9000 tons a year." This is a gross variation of 40 per cent; plainly, an unsatisfactory figure upon which to plan a chemical production program. Available supply can hardly ever approximate so uncertain and variable a demand. Since only by violent means can price serve to adjust such great variations in requirements, therefore insecticide prices are infamous for their instability.

Prices and Price Policies—The base line of prices is drawn by the cost of production. If there is no profit in producing any goods, the supply will gradually dry up. But the base of prices is not set by the most efficient, fortunately located, brilliantly managed plant. Without the output of the higher cost producers, supply would be inadequate and society must accordingly pay to keep them in business. The marginal producers are those whose output is necessary to meet the demands of the market. Marginal costs are the costs of those makers just able to produce at a profit. In the long run herein lies the base of the minimum price.

The costs upon which chemical prices are predicated are complicated by that production of joint products and by-products which characterizes all chemical operations. It is necessary to allocate various items of cost over two or more products, a practice that depends upon judgment, expediency, or policy rather than upon any established and recognized accounting practice. This obviously introduces a further complication into the variation inherently existing in chemical costs due to optional processes and materials or to varying yields. This distribution of costs affects not only the direct, but also the indirect costs, as follows:

Material Costs: Direct, the actual raw materials used in the processes; and Indirect, the supplies of coal, water, gas, lubricants, etc.

Labor Costs: Direct, operators and helpers engaged in operating the processes; and Indirect, the superintendents and foreman, maintenance crew, time keepers, watchmen, stores clerks, accountants, etc.

Manufacturing Costs, including General Overhead, which comprise the general service costs of power, heat, light, loss and spoilage, general administration, research, etc., and the General Fixed Charges of rent, interest on investment in plant and equipment, depreciation on the same items, insurance, taxes, etc.

Over and above these costs of production the expenses of containers, of handling, selling, packing, and of shipping and freight equalization, must all be reckoned with in setting the price of chemicals, and without going into a detailed discussion of the theories of cost accounting and the practices of bookkeeping, which would be out of place in this survey of the broad economic pattern of the chemical industry, it is to be noted again, that what portion of all these chargeable expenses shall be allocated to each of the several products of any given chemical operation introduces into chemical pricing fluctuating elements wholly within the control of management.

In actual sales practice these voluntary variations in the methods of cost finding have aggravated the involuntary variations in chemical costs to exert a considerable pressure upon prices. This pressure has undoubtedly influenced the pricing and selling policies of all chemical manufacturers who as a group are committed to the merchandizing philosophy of increased profits through increased volume of sales and who have learned that the only way appreciably to increase the demand for chemicals is so to lower the price that new uses as well as increased use by old customers expand the consumption. The industry's record shows that this is an economically sound theory of abundance.

While increased volume of output has been reflected in lower costs of production, it has not reduced the costs of distribution. In fact, in common with most industries, chemical manufacturers have discovered that since the First World War their sales and shipping expenses, as well as their taxes, have been increasing. The Robinson-Patman Law, with forced analysis of production and distribution costs, emphasized the auxiliary costs of sales.

Marketing Utilities—As the economic purpose of manufacturing is to increase the form-utility of goods, so the service of marketing is to enhance the utilities of time and place. Sulfur at the mine in Texas must be brought to the factory in Ohio before it can be used in vulcanizing rubber. This involves a great deal more than the act of selling to the rubber company's purchasing agent, yet this actual sale so arrests the attention that it overshadows the other services involved in distribution. At a time when the entire distributing system is under critical examination it is well to keep in mind all its functions:

1. *Assemblying* is "the seeking out of sources," the collection of raw materials, equipment, and supplies at a plant for use in manufacturing or by a jobber at a warehouse for re-sale.
2. *Storing* is "the depositing or holding of products in some place where they may be obtained at some future time," which includes stocks held at centers of consumption for the convenience of buyers, and stock accumulated during off-seasons of demand for the benefit of the maker.
3. *Grading* is the sorting of products according to trade specifications, a function which in the chemical industry is commonly associated with production, where the different grades, based upon chemical content, are a part of the making operation.
4. *Dividing* is breaking a commodity up into smaller lots for the convenience of the user, as when a jobber sells individual drums of material that he has taken in in carload lots or when a pharmaceutical house sells borax in small containers which it has bought in bulk.
5. *Packaging or packing* is sometimes akin to dividing, but in no instance can a chemical product be sold, as it were, "on the hoof," it must always be delivered in some sort of a container, be it an ounce vial or a tank car.
6. *Transporting* as a part of distribution is the physical moving of goods from producer to consumer, a complicated and important function in the chemical field.
7. *Selling* is the actual act of sale which is in turn broken down into four steps: (1) creating the demand, (2) informing the buyer of the kind, quality and quantity of the goods and the source of their supply, (3) determination of the price, (4) agreement upon terms.
8. *Financing* is the bearing of all the expenses of all of these different steps in marketing. It includes the not inconsiderable element of risk, not only in the good faith and ability-to-pay of all buyers, but also any chances that may be incurred in a decline in price or in the cancellation of orders.

THE STRUCTURE OF CHEMICAL INDUSTRY

Chemical Industry Classified—With the basic conditions which distinguish chemical production and distribution clearly before us we can now classify the industry and summarize its economic functions. This is the industry which produces commodities that differ chemically from the raw material out of which they are made. Lest the cook who boils eggs and the mason who slakes lime should be tempted to set themselves up as chemical producers, we must add that these chemical changes must be wrought by chemical means and under chemical control. This definition, borrowed from the late Dr. Teeple, makes the identification of a chemical enterprise quite simple.

Sulfuric acid from brimstone, alcohol from either molasses or ethylene, alum from bauxite, alizarin or aspirin from coal-tar—all these are plainly chemical operations. Moreover, gun cotton and Bordeaux mixture, baking powder and straw hat cleaner, tincture of iodine and Eau de Cologne, though not usually considered products of the chemical industry, are nevertheless indubitably chemical products. Accordingly, the chemical industry divides itself naturally into two distinct parts:

1. *The Chemical Producing Industry* which manufactures all sorts of chemical products from superphosphate to plastic molding powder.
2. *The Chemical Converting Industry* which makes chemical products into all sorts of consumer goods from a mixed fertilizer to an imitation amber cigarette holder.

Beyond these two classes of the chemical industry proper is the great group of industrial consumers of chemicals:

3. *The Chemical Processing Industries* which employ chemicals as tools to change or modify natural raw materials to adapt them better for human use, as in the manufacture of leather, rubber, textiles, etc.

Clear-cut distinctions mark these three groups, and these distinctions are important. Chemical products are a vital element in our national industrial structure. Notably this is true since synthetic materials have invaded big markets long securely held by natural products from farm and mine and so disturbed the established order in many an old fabricating field. Viewed objectively sodium nitrate from Chile and from Hopewell is not the same material, and this distinction is quite serious in chemical, or commercial, or political considerations.

Furthermore, the chemical industry has become a "public industry." Its key position in peace and war is appreciated by statesmen and generals, by economists and businessmen. More than this, our leading chemical companies are no longer family-owned enterprises. Their shares are freely traded in and widely held. Therefore the "statistical position" of chemicals is today something much more than a glib phrase in a trade paper market report, and the lazy habit of throwing all the chemical making and converting and processing industries into a single group as the so-called "chemical processing industries" becomes dangerously misleading.

Such a blanket classification smothers fair comparison. It combines not only chemical plants and pharmaceutical factories, but also coke ovens and candy kitchens, soap works and dairies; industries so distinct in their economic position, in their raw materials and apparatus, in their capital structure, in their consuming fields and marketing methods that to regard them as a group is like the proverbial comparison of cheese with chalk. If, however, the threefold classification above is recognized, it clarifies a complicated economic group since each division possesses significant, common characteristics.

Chemical Producing Industry Defined—The Chemical Producing Industry is small numerically, but generally composed of large units. It manufactures over five thousand distinct chemical items which today include a host of synthetic raw materials, not only dyes, flavors, medicinal chemicals, but also fibres, resins, plastics, rubber substitutes, and what not. Within this group are commonly placed a group of natural raw materials, such as sulfur, salt, naval stores, borax, which are not manufactured, though their uses are chemical.

The basic chemical products are in the main industrial raw materials and well over 90 per cent of the output is consumed by the chemical industry itself in further chemical operations and in chemical converting into consumer goods. These products are produced by chemical reactions in distinctively chemical equipment, often in vast tonnages, and they are shipped in bulk containers. The entire group, as we have seen, is characterized in its production operations by varying yields and fluctuating costs, by-products and wastes, new processes and new products, by high obsolescence and excessive depreciation; and in its distribution field by producing a great number of products, each of which usually has many markets. Hence within this group research is a necessity and progress is highly accelerated.

The Converting Industry—Within the second group, the Chemical Converting Industry, are the makers of medicinal and cosmetic preparations, fertilizers and insecticides, explosives, coatings, soaps, refrigerants, liquid and gaseous fuels, etc. Within this group fall the molders and laminators of plastics. Here, too, is found the growing group of chemical specialty manufacturers.

Upon the basis of their marketing fields the last may be subdivided into the makers of industrial, household, and agricultural specialties. For the industries they compound wetting-out agents, emulsifiers, driers and solvents, accelerators and inhibitors, abrasives, adhesives, and polishes, bates for tanning, special oils to soften leather, to pull wire, to dress belting, to make fibres more spinnable, to prevent rust; thousands of chemical compounds used by all sorts of factories to make goods better and more usable, more durable and less expensive. For the public the specialties makers produce polishes for metals, furniture, marble, shoes, automobiles; cleaners for drains, for rugs, wallpapers, clothing, and hats; water softeners, insecticides and moth repellents; radiator cleansers, anti-freeze mixtures, top dressings for motor cars. Farmers, orchardists, and gardeners now all have their own chemical specialties in fertilizers, insecticides and fungicides, even in vitamins, plant hormones, and nutrient solutions.

This chemical converting group is heterogeneous, with many subdivisions, composed of big and little units, distinguished by the fact that they are preparing chemical compounds for the direct use of an ultimate consumer. Outside the chemical industry itself they are, as a group, the largest consumers of chemicals which they mix, manipulate, and compound. It is significant that chemical producers are invading this converting field and making more and more specialties for sale direct not only to the industries and the farms, but also to the general public. In itself this is a major commercial revolution in chemical distribution. It bespeaks a profound change in the selling point of view, and in the years to come will radically change chemical manufacturing and merchandizing methods.

What Is a Processing Industry?—The third group, the Chemical Processing Industries, are chemical only incidentally. Rubber vulcanization, leather tanning, the transformation of fibre into cloth, of iron into steel, of silica into glass, are all operations involving much chemistry and employing many chemicals. They are not, however, chemical operations.

These industries treat their own materials by various chemical processes; but both in their purchase of chemical supplies and their use of chemical apparatus, this processing is but one step in the series of their distinctive production operations. A woolen mill, for example, scours, softens, bleaches, and dyes. For these operations it buys chemicals and chemical specialties in considerable quantities. Much of the great recent progress in new and improved fabrics has come from new fibres and new chemical treatments introduced by chemical research done by the chemical companies. But the chief raw material of the woolen mill is wool. Its great capital investment is in spinning and weaving machines. Its finished product is woolen cloth. Thus the manufacture of rubber, steel and alloys, paper, glass and ceramics, textiles, leather, all involve the chemical processing of some important natural products: latex, ores, wood-pulp, sand and clay, cotton, flax, silk, rayon, or hides, etc. These processing industries, while heavy consumers of chemicals, are not a part of the chemical producing industry, but its customers. They never identify themselves with the problems or interests of the chemical manufacturing industry.

Applied Chemical Economics—In the following pages the materials and techniques employed in the chemical producing, converting, and processing industries will fill in the foreground of the broad economic pattern we have outlined for the entire group. We have sketched that economic background in a few bold strokes, indicating the chief and unique points which distinguish the industries employing chemical means to make their products more useful, more durable, more beautiful, more adaptable to the use of mankind. The surveys of the more important items of the technical picture in each field that comprise the chapters of this book are, from this point of view, case studies in applied chemical economics in the department of production.

Expansion in these chemical industries has been almost explosive. Particularly in the past twenty years this prodigious growth has brought its troubles to those who wish to acquire knowledge of the more important phases of chemical industrial activity. The field is now so immense that those closely associated with it are perforce tending to "learn more and more about less and less." Such specialization has become inevitable. Nevertheless, every alert person has need of sources of information which give a broad overview of the entire chemical realm and which indicate the sources of specific information which may be consulted for greater detail. At the very foundation of any industrial operation undertaken in expectation of profit are economic considerations which in the last analysis determine the right answers to all the other questions, technical or commercial, that are daily coming up for decision. By definition, therefore, a thorough understanding of the principles of chemical economics is the proper introduction to such a survey of the technique of chemical producing and processing as the following chapters present.

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CHAPTER 2

THE UNIT OPERATIONS

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Every long established craft, art or specialized industry employs certain tools and certain pieces of equipment which are so characteristic that they may serve as trade marks of the calling. But when chemical industry began to come of age the pattern of equipment which it used seemed to reflect adolescent confusion. The welter of things which were used to promote the various processes, seemed to have "just growed." There was little evident unity of pattern, either in function or design. One who studied the ways and means of carrying out the various chemical processes was confronted with as much confusion as students of botany must have been in those early days before any one had ferreted out the natural organization, and devised a rational scheme of classification of living species.

The more the new developments crowded into the realm of chemical industry, the more necessary it became to put the study of the complicated field on a rational and well-organized basis. From this necessity rose the field of knowledge which is now designated as "chemical engineering," which, in essence, is the application of various branches of science to the problems of chemical industry. The field can hardly be defined completely or exactly but the frame work of the structure has evolved along two main lines: "The Unit Operations" and "The Unit Processes."

The unit operations are confined to the various physical operations which are common to a great variety of chemical processes: evaporation, distillation, filtration, heating and cooling, crystallization, gas absorption—operations which are encountered in every chemical laboratory and in every chemical manufacture. Later, the Unit Processes came into being as a systematic approach to the important aspects of particular types of chemical reactions which are industrially important. These are discussed in Chapter 3.

It would be a serious error for anyone to assume that the whole story of chemical industry can be told within the quantitative framework of present day chemistry, physics, the unit operations and the unit processes. Much of the attitude and inexact knowledge of the old industrial arts still survives in many branches of the industry. Although each year sees more and more exact knowledge brought to bear on the problems of the industries based on chemical reactions, old time craftsmanship, crude empiricism and, unfortunately, secrecy still play important roles in many cases. This merely means that chemical industry is still in its infancy and the field has the possibilities for tremendous advancement for many years to come. The remarkable progress of the past few decades has been due to a large degree to the application of the systematic knowledge of the unit operations to the old fields where crude empiricism and secrecy reigned. Hence, it is essential to present, in brief outline, the principal points of the subject.

Pattern of Presentation—The pattern of presentation of knowledge in the field of the unit operations is one of functionalism. The student of apparatus centers his attention on the *function* of the equipment. The form it takes is merely a feasible adaptation of apparatus to certain principles. This has brought into clear focus the underlying physical principles which are common to many processes and dozens of different types of equipment. There is nothing essentially new in this approach. It has been applied to many fields of knowledge, both in the field of science and elsewhere. It doesn't bring simplicity to a field which is so complex that it cannot be simple, but it does substitute order for confusion.

The space which can be allowed for the subject in this book limits the presentation to something which is not much more than a cataloging of the functions, with several illustrations of typical pieces of equipment.

This chapter will be devoted to the most essential descriptive aspects of the following unit operations:

Fluid Flow
Heat Transfer
Evaporation
Crystallization
Distillation
Drying
Air Conditioning
Gas Absorption and Desorption
Extraction
Filtration
Crushing and Grinding
Separation of Solid Materials

For those who are interested in pursuing the quantitative aspects of these various operations, there are numerous books and magazine articles which are worthy of study. Several of them are found in the Reading List at the end of the chapter.

FLUID FLOW

Most plants which are connected, even remotely, with chemical industry are so filled with pipes and valves that they strike the uninitiated as being the work of a plumber gone wild. But the standard plumbing equipment does not fill all the requirements. Conduits range in size from tubes of capillary dimensions to gas mains ten feet in diameter. They may be standard pipe, seamless tubing, rectangular air ducts, or variations or combinations of these.

The materials of construction show as great a range of variation of size and shape. In addition to certain strength requirements, the need of resistance to almost every form of corrosion must sometimes be met. Though iron and steel, of course, account for the bulk of the construction, chemical industry has to use a variety of other materials. Brass, bronze, stainless steel, a multitude of alloy steels and irons, copper, tantalum, aluminum, silver, zinc, lead, glass, rubber, ceramic ware, asbestos, amorphous carbon, graphite, and plastics all have their place in conduit construction; and the list is by no means complete.

Measurement—In earlier days, plant measurement and control of fluid flow were left pretty much to guesses and crude estimates, but now accurate instruments have all but completely replaced operators' uncalibrated judgment in the matter of measurement and, to a large extent, in control. The principles and types of instrumentation are dealt with in another chapter.[1]

Pumps—The fluid pressures encountered in chemical industry may vary by a million-fold—from a thousandth of an atmosphere to a thousand atmospheres. Fluid temperatures range from those of liquid air to perhaps 1200° F. Corrodibility may be negligible, or it may be so great that the expression "nothing will hold it" is almost literally true. Liquids may be as clean as distilled water or they may be heavy sludges of highly abrasive grit. But there must be pumping devices to meet all these conditions, for wherever a fluid is flowing something must have been used to give it the necessary impetus. A book devoted to descriptions of all available pumping devices would be as large as the catalog of a mail order house. It would have to deal with an almost endless variety of blowers, vacuum pumps, ejectors, piston pumps, centrifugals, air lifts, acid eggs, gear pumps, volute and turbine pumps, of a variety of sizes and materials of construction.

These short paragraphs merely catalog the functions which fluid flow devices must fulfill. It is not one of the purposes of this book to go into a discussion of the laws of fluid flow. Also it would be pointless to present a picture of a piece of pipe and of a particular pump, for they would divulge nothing that is typical or important to the whole field. So fluid flow is left with this casual treatment but that should not be taken as a measure of its importance. It is very important and fundamental, and is a basic part of almost every process in the chemical industry.

The great body of qualitative and quantitative information available upon the pumping, storage, and transfer of fluids will be found in numerous articles, text books, hand books, and manufacturers' catalogs, a number of which are listed at the end of the chapter.

THE FILM CONCEPT

One of the most useful concepts in chemical engineering is that of the presence of a stagnant film at the phase boundary of any moving fluid. Whenever a gas or a liquid moves over a solid surface, or a gas moves over a liquid, a static film of the moving substance clings to the surface of the stationary one. This film greatly slows down the transfer of material or energy from one phase to the other, because all transfer of molecules through the stagnant film must be by the slow process of molecular diffusion. The transfer of heat through such a film is by the relatively slow mechanism of conduction through a fixed body.

A great deal of academic energy has been expended in the past, arguing about the reality of such films; some contending that the stagnant layers are real and of finite thickness; others believing that the films are mere convenient hypotheses. The truth of the situation seems to have been well established by careful measurements of fluid flow through conduits.[2] The interpretation of the evidence is that, at a phase boundary, there is a microscopic film, probably not more than a few molecules thick, which is truly stationary. Outside of this the fluid layers move along slowly, parallel to the boundary.

[1] See Chapter 5.

[2] Stanton, Marshall and Bryant, Proc. Royal Society. Sec. A. *97*. 413 (1920).

In cases of slow flow, these parallel lines persist throughout the conduit. When the overall velocity is great, the parallel flow is broken up a short distance from the boundary and the fluid moves forward in turbulent swirls. This layer of fluid next the wall, moving in slow parallel flow, is the film, which, though not quite stagnant, does slow up the transfer of energy or material from one phase to another. No matter how great the velocity and turbulence in the main stream, this slow moving layer is always there. Careful measurements have shown that in the case of gas flowing rapidly through conduits, this film thickness is of the order of a relatively few thousandths of an inch. The thicker this film, the greater its resistance to the transfer of either molecules or energy. Where rapid rates of transfer are desired it is necessary to cut down the film thickness as much as possible. Increasing fluid velocity or decreasing viscosity are two of the most effective methods of doing this.

The widespread utility of this film concept will be evident as the different operations and the equipment for carrying them out are discussed. The concept is especially useful in considering a great many of the phases of chemical engineering. It enters with especial prominence into such operations as heat transfer, gas absorption, liquid-liquid extraction, dehumidification, etc.

HEAT TRANSFER

It is only necessary to compare the efficiency of the cooling system of a modern automobile with that of an old Model-T Ford to have an illustration of the recent advances in the field of heat transfer. At the time of the first successful airplane flight (in 1903) the difficulties of dissipating the heat generated in a modern 2000 horsepower air-cooled aviation engine would have seemed insurmountable to even the best engineer. Less spectacular and less known, but equally significant, advances have been made in the multifarious pieces of heat transfer equipment in chemical industry. The transfer of heat from one substance to another is of such universal importance in nearly all processes, that this subject is one of the basic tools of chemical engineering.

Functions of Heat Transfer—There are two outstanding functions which heat transfer equipment serves: (1) to conserve heat energy, (2) to maintain a required temperature in a given piece of apparatus.

An example of the first item is usually found in properly designed distillation equipment. The vapor leaving the top of a distilling column must be condensed, usually on tubes which are cooled with water flowing through them. This water leaves the condenser at an elevated temperature and is used to preheat the feed liquid coming to the still.

An example of important temperature control is found in the nitration[8] of benzene. Considerable heat is evolved but the temperature of the reacting liquid must be kept below 60° C., for safety reasons. Thus, in every nitrator, there is a more or less elaborate system of cooling coils, through which water is circulated to keep the temperature down.

Every piece of refrigerating apparatus involves heat transfer equipment. Chemical industry uses a multitude of jacketed kettles of various kinds. A heat transfer medium; it may be steam, hot water, hot oil, molten salts, organic

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[8] See Chapter 3.

liquids, or a refrigerated brine, is circulated through the jacket to maintain a desired temperature, either above or below that of the surroundings.

The United States is a country with unparalleled fuel resources, so energy is generally considered an inexpensive commodity. For that reason, the use of expensive heat transfer equipment for purposes of conserving energy was rather slow to develop here. In earlier years the engineers of some European countries studied the problem much more thoroughly than did the Americans. But American experience finally demonstrated that though energy may be cheap, it is often too expensive to be thrown away. Every modern chemical plant has become conservation-minded and has gone into the business of saving heat units wherever possible. And it pays.

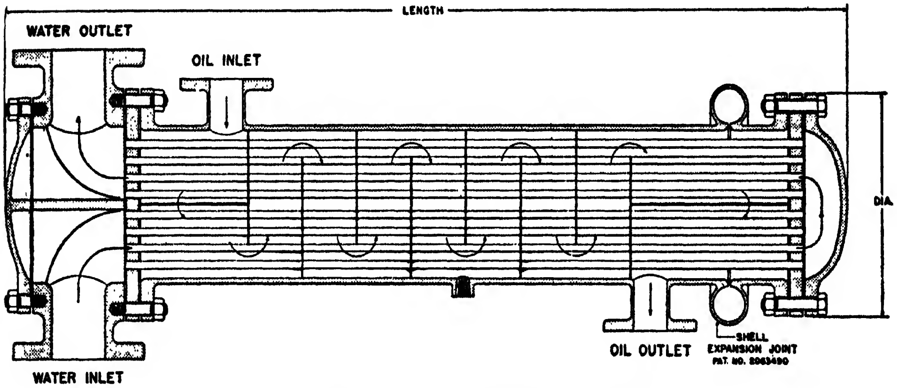

FIG. 1. Cross Section of Oil to Water Shell-and-tube Heat Interchanger. (Courtesy Davis Engineering Corp.)

Films in Heat Transfer by Forced or Natural Convection—The film concept has been of paramount importance in putting the study of heat transfer on a scientific basis. In the majority of cases in the chemical industry, the transfer takes place between two fluids separated by a thin metal wall. One fluid may be used to heat another; condensing steam, to heat a gas, water to condense steam, etc. In such cases the major resistance to heat transfer usually resides in the minute fluid film which clings to the metal walls. The realization of this fact brought about great changes and improvements in the design and operation of the equipment.

The thickness of a fluid film is greatly decreased by increasing the velocity of a fluid through a conduit, and to a certain extent by decreasing the conduit diameter. Although the exact relations between variables in heat transfer are too complicated to be summarized briefly, it is approximately true that for fluids passing through conduits at a fairly rapid rate, the coefficient of heat transfer[4] varies as the 0.8 power of the mass rate of flow of fluid, and inversely as the 0.2 power of the conduit diameter. Hence, for liquid-liquid heat exchangers it has been found advantageous to build the apparatus so the fluids will pass rapidly through small-diameter conduits. The compact, modern heat interchangers transfer a surprising amount of heat in a small space. The con-

[4] In the English system the film coefficient of heat transfer is: B.T.U. per hour per square foot of heating surface per degree F. temperature difference.

struction of a well designed widely used type of "shell and tube" heat exchanger is illustrated in Figures 1 and 2. Other types of heat transfer apparatus include pipe coils, long double pipe exchangers, a multitude of special conduit shapes, jacketed vessels, etc.

The important factors, other than fluid velocity and conduit diameter, in determining the rate of heat transfer in forced convection are the viscosity and coefficient of thermal conductivity through the stagnant layer. If the rate of fluid flow through a conduit is fairly rapid then the film coefficient of heat transfer varies approximately as the 0.6 power of the coefficient of thermal conductivity and inversely as the 0.4 power of the viscosity. Hence, for viscous fluids with low thermal conductivities, such as some oils, much more surface must be provided to transfer a given amount of heat than is required for a liquid such as water.

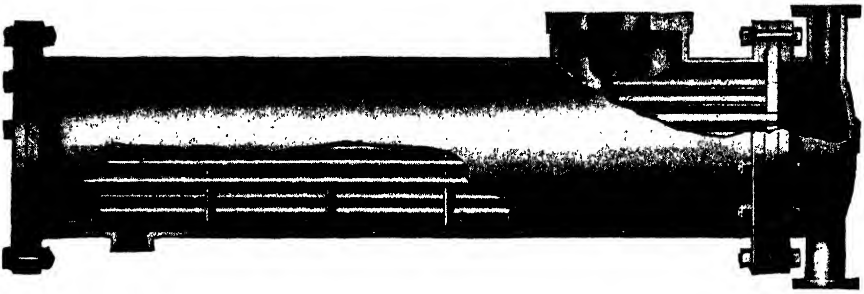

FIG. 2. Cutaway View of Shell-and-tube Heat Exchanger Showing Construction. (Courtesy Ross Heater and Mfg. Co., Inc.)

The quantitative relations of the important variables in the various cases of heat transfer can be found in publications listed in the Reading List at the end of this chapter.

Magnitude of Film Coefficients—In engineering practice, film coefficients of heat transfer are usually expressed in the units: B.T.U. per hour per square foot per degree F. Many things affect the value of these coefficients, such as: rate of flow of fluid, physical character of fluid, temperature, etc. But for different types of fluid there are approximate ranges of values of the transfer coefficients. Table 1 gives compilation of these approximate ranges of values as met in practice.

TABLE 1—RANGE OF VALUES OF MISCELLANEOUS FILM TRANSFER COEFFICIENTS AS FOUND IN PRACTICE*

Type of Fluid	*K*† *Free Convection*	*K*† *Forced Convection*
Water	50–150	300–1000
Oil	5–10	10–75
Boiling Water	300–1000	1000–1500
Condensing Steam	800–3000	
Condensing Organic Vapors	50–500	
Gas (atmospheric pressure)	0.5–1.5	2–10

* Compiled largely from data reported in Perry, S. H., "Handbook of Chemical Engineering," 1st ed., Section 7, McGraw-Hill Book Co., New York (1934).

† Film coefficient of heat transfer. B.T.U. per hour per square foot per degree F.

Because of the magnitude of the resistance to heat transfer encountered in most fluid films, the presence of a thin metal wall separating two fluid phases has but relatively little effect on the overall rate of heat transfer in most equipment. This generalization is not true if very thick metal walls or glass or stoneware separates the two phases.

Methods of Providing Maximum Surface—If two fluids are passing through a heat transfer apparatus, the resistances of the two films are operating in series, exactly analogous to two electrical resistances in series. Inspection of Table 1 will show that any device which is used to heat a gas such as air will have a low overall coefficient of heat transfer, no matter what the heating fluid may be. An obvious way to partially counteract the low coefficient of a gas film is to provide a large amount of contact surface on the gas side of the apparatus. The naturally evolved form of apparatus for this condition, is a tube covered with thin metal fins to provide large contact surfaces. This is seen in various modifications in automobile radiators and also in a great many pieces of industrial equipment. A typical air heater which provides large area by metal fins is shown in Figure 3.

FIG. 3. Three-inch Radiafin Tube. (Courtesy Schutte and Koerting Co.)

Effect of Scale—Just as a very thin stagnant film of fluid offers a great deal of resistance to heat transfer, so does any thin layer of scale on a pipe wall greatly slow down the rate at which heat may be transferred. It is fruitless to have conditions which are conducive to high transfer coefficients through the fluid films, if the pipe wall is covered with a substantial layer of scale. As heat transfer studies have advanced, leading to higher and higher film coefficients of heat transfer, the combating of scale formation has taken on new importance.

Scale is here interpreted in its broadest possible sense and may be a layer of rust, a layer of calcium sulfate inside a boiler tube, a coating of oil, or any of a large variety of materials which may adhere to tube walls. The more engineers have become engrossed in efficient heat transfer equipment the more they have had to combat scaling in its various forms. Corrosion resistance has become of paramount importance. This has brought a multitude of corrosion resistant alloys and other materials of construction into use. Cleanliness has taken on new meaning. Relatively small amounts of impurities in water or other heat transfer media may render heat transfer equipment almost unusable. The complicated treatment of feed water for modern high pressure boilers illustrates the importance of the presence of small amounts of impurities.[5]

Dropwise Condensation—If the idea of the desirability of extreme cleanliness is carried over to the phenomenon of condensation an apparent paradox appears. It has been found that uncontaminated vapors condensing on a very

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[5] See Chapter 6.

clean surface sometimes give very much lower coefficients of heat transfer than when the vapors and surfaces are contaminated with certain organic impurities.

This phenomenon has been carefully investigated[6] and it has been found that the coefficient of heat transfer, and hence the rate of condensation, is greatly increased if surface conditions are such that condensation occurs in small drops rather than in a thin, uniform film over the whole surface. This type of condensation is greatly affected by interfacial tension between the solid and condensed liquid. It is found that certain organic molecules which orient themselves on the metal surface promote dropwise condensation and hence high coefficients of heat transfer for this case. Mercaptans for copper, and fatty acids for iron have this property to a marked degree. Small amounts of lubricating oil in condensing steam tend to cling to the solid surface, and have a beneficial effect in promoting dropwise condensation. Hence, for the phenomenon of condensation, the ideal of a perfectly clean and uncontaminated system is not quite valid.

Nuclear Boiling—A condition somewhat analogous to dropwise condensation is encountered in boiling. The familiar phenomenon of a drop of water dancing on a hot metal plate and evaporating very slowly indicates the effectiveness of a stagnant vapor film in slowing down the rate of heat transfer. This case where a stagnant vapor film persists between a hot metal surface and a boiling liquid is designated as "film boiling" and is definitely undesirable because of the low coefficient of heat transfer. This film boiling will occur,[7] for nearly all liquids, if the temperature difference between the metals surface and the liquid is greater than about 50° F. If the temperature drop from the tube surface to the liquid is less than this, "nuclear" boiling is maintained, wherein the vapor bubbles rise from nuclei on the surface without the presence of the continuous film which blocks rapid heat transfer. Hence, very large temperature differences in apparatus where boiling occurs are undesirable. It has been found that, in some cases, the boiling of a liquid is actually slower with high steam pressure in a heating coil than if low pressure steam is used.

As in the case of condensation, the manner of boiling is affected to a considerable degree by the character of the surface.[8]

Heat Transfer by Radiation—Heat transfer by radiation is a phenomenon which cannot be fitted into the film concept. Radiation is a unique form of energy which is readily converted into heat if it is "absorbed" by a substance; gas, solid or liquid. Conversely, hot gases, solids or liquids, except in a few special cases, emit radiant energy.

It is safe to assert that practically all of the energy we utilize in the world has at some time been in the form of radiation. All the energy stored in fuel was at one time radiant energy coming from the sun, and the water for hydroelectric power was evaporated by the heat which came from the sun's rays. When coal, wood, oil or gas are used as fuels they are burned, and a large part of the energy is transmitted by radiation to some heat receiving surface, such as

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[6] Nagle, W. M. and Drew, T. B., Trans. Amer. Inst. Chem. Engrs. *30*, 217 (1934); Nagle, W. M., Bays, G. S., Blenderman, L. M. and Drew, T. B., ibid. *31*, 593 (1935); Drew, T. B., Nagle, W. M. and Smith, W. B., ibid. *31*, 605 (1935).

[7] Akin, G. A. and McAdams, W. H., Trans. Amer. Inst. of Chem. Engrs. *35*, 137 (1939).

[8] Rhodes, F. H. and Bridges, C. H., Trans. Amer. Inst. Chem. Engrs. *35*, 73 (1940).

boiler tubes. As chemical industry has become more widespread it has gone into more fields of endeavor and heat transfer by radiation has become an increasingly important item. Wherever hot fuel beds, electric radiant heaters, flames of oil, gas or powdered fuel are used for heating, heat transfer by radiation is an item of outstanding importance.

Principles of Heat Transfer by Radiation. The amount of energy which a body will emit or receive depends upon the temperature and upon the character of the surface, if it is a solid, or the internal condition, if it is a liquid or a gas. The temperature effect is summarized by the Stefan-Boltzmann law which states that the amount of heat radiated is proportional to the fourth power of the absolute temperature, and that the net amount of interchange of radiant energy between two bodies at different temperatures is proportional to the difference between the fourth powers of the absolute temperatures of the two bodies. The absorption coefficients of the respective bodies also play a major role in determining the amount of energy exchange. In addition, the relative arrangement of the surfaces has a large effect, so a problem in radiation necessarily involves geometric factors.[9]

One unique feature of radiant heat transmission is that the energy can be effectively transferred at a distance. The best example of this is seen in the fact that the earth's ultimate source of energy, the sun, is about 93,000,000 miles away. This ability to transfer energy at a distance is used in the construction of boiler furnaces, petroleum cracking units, etc., by providing large combustion spaces for release of energy from hot flames. If high temperature flames impinge directly on metal surfaces, the metal is quickly melted or oxidized and rendered useless. But if the hot flames are kept some distance away, by being released in a large combustion space, the heat is transferred from the flame to the wall at a moderate rate and the metal does not become overheated. Hence, in contrast to the compact construction of convective heat interchangers (see Figures 1 and 2), apparatus for radiant transmission is built with large open spaces, as shown by the diagram of the combustion space in Figure 4.

Radiation Plus Convection. In industrial equipment heat transmission by radiation seldom, if ever, functions alone. In apparatus in which a gas or liquid is present there is necessarily some transmission by convection and conduction as well. In general, apparatus is usually built so most of the transmissions at very high temperatures will be by radiation, while the bulk of the transfer at moderate or low temperature will be by convection and conduction. In a furnace, such as a powdered coal boiler furnace, where heat is being transferred from a flame, the apparatus is usually arranged so 40 to 50 per cent of the energy released will be transmitted to the apparatus by radiation, the remaining recoverable heat being picked up in a convection section of boiler tubes.

The Use of Regenerators—In the case of such pieces of apparatus as by-product coke ovens or open hearth steel furnaces it is necessary to obtain high flame temperatures by pre-heating the air which is used for combustion. The pre-heating of the air is commonly accomplished by passing it through a "regenerator" made of a checker work of brick. The brick are first heated by

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[9] Hottel, H. C., "Second World Power Conference," *18*, Sec. 32, No. 243 (1930); Mech. Eng. *52*, 699 (1932); Trans. Amer. Soc. Mech. Eng. F.S.P. *53*, 19b, 265 (1931).

passing hot flue gases through the checker work for a certain period of time. Then the cycle of operation is changed; the air for combustion is pulled through the hot checker work and the flue gases leave through another regenerator section.[10] The length of the cycle for satisfactory operation depends primarily on the size of the regenerator and the rate of driving the furnace.

This method of heat recovery not only permits the attainment of much higher flame temperatures but also effects major heat economies. It was first developed for use in connection with steel furnaces and has found numerous applications in other branches of industry.

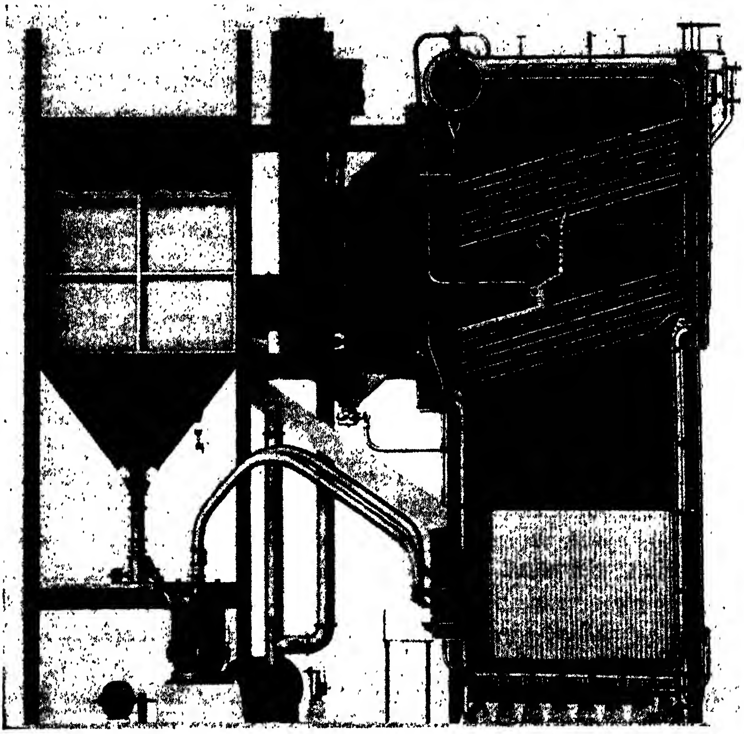

FIG. 4. Powdered Coal Boiler Furnace. Note large combustion space where heat is transferred to tube surfaces, largely by radiation, and the large number of tubes provided for transfer by convection in those parts of the furnace where the tubes cannot "see" the flame. (Courtesy Babcock and Wilcox Co.)

Status of Knowledge of Heat Transfer—Literally thousands of pieces of research have been carried on in connection with the various phenomena of heat transfer. As a result, fairly accurate predictions can now be made on the performance of most types of systems and equipment. This has resulted in innumerable economies in heat conservation throughout industry and has greatly improved accuracy of temperature control and efficiency of operation in other ways. In the field of heat transfer, particularly, fundamental studies have led to great practical benefits. In the flow sheets and descriptions of the various

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[10] See Chapter 23.

industries discussed in this book, the reader will repeatedly see the results of the application of this fundamental knowledge.

EVAPORATION

The evaporator is essentially a device for increasing the concentration of a solution by the evaporation of water. It finds its largest use in such industries as sugar,[11] salt,[12] and caustic.[13]

Reduced to its fundamentals, the problem of evaporation is one of finding the mechanically best and most efficient means of transferring approximately 1000 B.T.U. per pound of water evaporated and disposing of the water vapor which has been released.

The simplest form of evaporator is an open pan filled with solution, with a fire under it, such as is still often used for making maple syrup. Such a device is inefficient and difficult to control. The direct fired open pan was once used extensively for salt production. It is now practically extinct in this country but is still employed to a considerable extent abroad.[14] Besides being inefficient and hard to control, a direct fired pan operates with high surface temperatures which can lead to the destruction of organic compounds present in the solution—due to overheating.

The evolution of the modern efficient evaporator is marked with at least three major and a number of minor improvements.

The Steam-Heated Open Vessel—The first of these improvements was the use of steam, in coils or jackets, as a heating medium. Despite the fact that this required separate boiler equipment, it improved efficiency and promoted accurate control of the evaporation operation.

Many chemical plants have numerous, small-scale evaporating jobs that can most feasibly be carried out in steam jacketed kettles, even though the steam economy may not be great. Although jacketed kettles are commonly constructed of iron or copper they are obtainable with corrosion resistant lining, such as nickel, stainless steel or enamels (glass lined). Whenever agitation is called for, this may be easily provided by an appropriate stirrer or agitator. In any case, agitation of the liquid increases the liquid velocity over the heated surface and thus increases the rate of heat transfer to the boiling solution; which increases the capacity of the apparatus.

An effective evaporator of this type may consist merely of an open tank with a submerged steam coil.

The most common large-scale, open-pan type of evaporator in use today is probably the salt "grainer."[15] This consists of a large flat pan with submerged steam pipes into which saturated salt solution is fed. As evaporation proceeds, salt crystals separate and these are raked out, along with a certain amount of the mother liquor. The mother liquor is drained off and returned to the pan. The chief advantage of such an outfit is simplicity of apparatus and operation. It also produces a type of salt grain which is particularly desirable for some purposes.

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[11] See Chapter 35.

[12] See Chapter 9.

[13] See Chapter 10.

[14] See Chapter 9.

[15] See Chapter 11.

Evaporation in Closed Vessels Under Reduced Pressure—The next step in the evolution of the modern evaporator was the enclosing of the vapor space above the boiling solution and removal of vapor by condensing it on an adjacent cold surface, either a tubular water-cooled or a water jet condenser. This results in evaporation under reduced pressure and hence at lowered temperature. The removal of vapor by a separate condenser necessitated the introduction of a means of removing the non-condensable gases from the system. This is accomplished by a vacuum pump or by the barometric leg or certain types of jet condensers. The principal result of these developments was to greatly increase the capacity of evaporators.

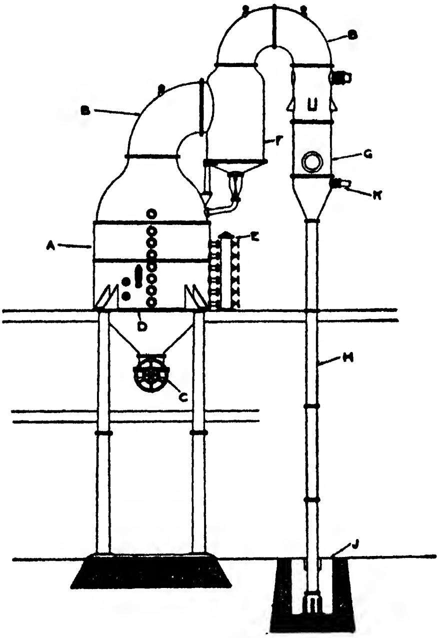

Fig. 5. Vacuum Pan. One type of single effect evaporator.

The essential features of such a single effect evaporator are shown in the vacuum pan, such as is used in the sugar industry.[16] (See Figure 5.)

The vacuum or strike pan is a cylindrical vessel, A, usually of cast iron, having a dome-shaped top with vapor pipe, B, and a conical bottom provided with a strike or discharge valve, C. It is equipped with large heating coils of copper, and steam vacuum gauges, also sight glasses, D, for watching the progress of work, and proofstick for drawing test samples. The steam enters a manifold, E, from which it is distributed to the coils; each of the latter has a stop valve for steam, and drainage connections for condensation water. The vapors from the boiling solution pass through a save-all, F, connection at the bottom of the pan, where they expand and meet baffle plates, so that material entrained with the vapor may be returned to the apparatus. The vapors from the evaporating liquor pass into a condenser, G, in which they meet a shower of water. The non-condensable gases are led off through a pipe, K, to a vacuum pump. The condensing water and water of condensation are carried off through the barometric leg or torricellian tube, H. The foot of the leg pipe is sealed with water in the hot well, J. One common type of barometric condenser is shown in Figure 6.

The removal of non-condensable gases, such as air dissolved in the water, is a most essential feature of such an evaporator. If they are not removed by some type of vacuum pump they quickly accumulate in the evaporator body and practically stop all evaporation. A reciprocating vacuum pump or a high velocity steam ejector is commonly used for this purpose.

One design of barometric leg acts as an effective ejector and removes the

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[16] For details of vacuum pan operation see Chapter 35.

non-condensable gases without the use of a mechanical vacuum pump. (See Figure 7.) Where the amount of non-condensable gases is small such a jet condenser will maintain a vacuum of 26 to 27 inches of mercury. The amount of water required for condensation of the vapors from an evaporator of course depends upon its temperature, but in practice an average of about 25 pounds of condenser water is required per pound of water evaporated.

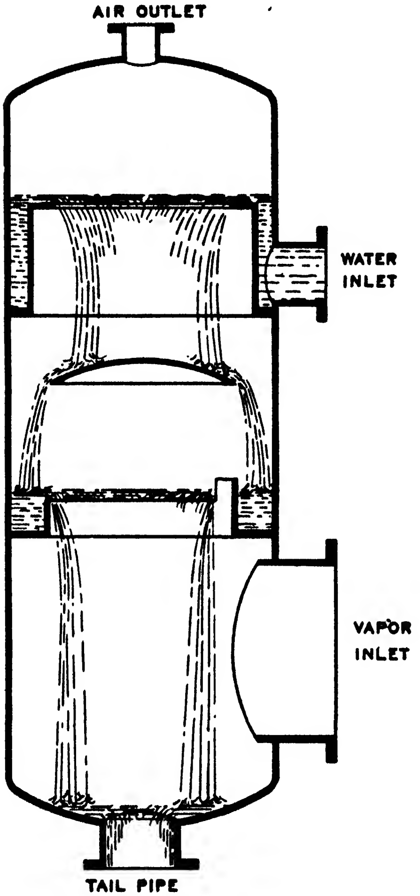

Fig. 6. Cross Section of Barometric Condenser. (Courtesy Struthers-Wells Co.)

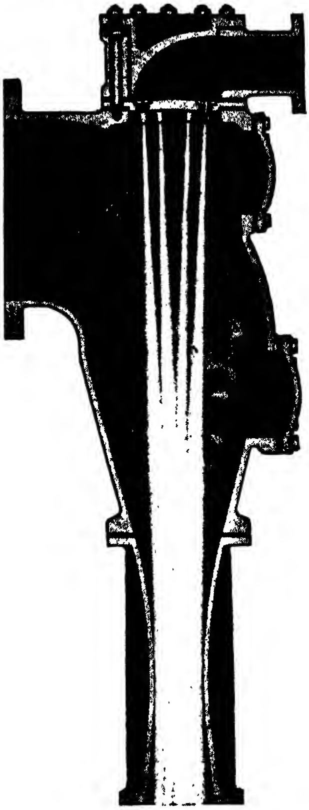

Fig. 7. Jet Condenser.

The arrangement described above mixes the condensate with the cooling water. In cases where it is desirable to save the condensed vapors, for instance in locations where fresh water is scarce, it is desirable to use a shell and tube-type of condenser. (See Figures 1 and 2.) The non-condensable gases are removed by a vacuum pump attached to the shell side of the condenser.

Although the vacuum pan described above is used primarily in the sugar industry, single effect evaporators which are the same in all essentials are used in other industries, particularly salt.[17] A diagram of a basket type evaporator with arrangement for removal of salt produced by evaporation is shown in Figure 8.

Multiple Effect Evaporators—The greatest improvement in the economy of evaporation came with the introduction of the "multiple effect" wherein the vapors leaving one evaporator body are used as steam to evaporate water in a second body, and so on, with sometimes as many as six effects operating in series. This requires that the pressure shall be successively lower in each succeeding effect. Although this calls for more equipment for a given capacity, as compared to a simple single effect evaporator, it greatly decreases steam consumption; as several pounds of water can be evaporated per pound of boiler steam used.

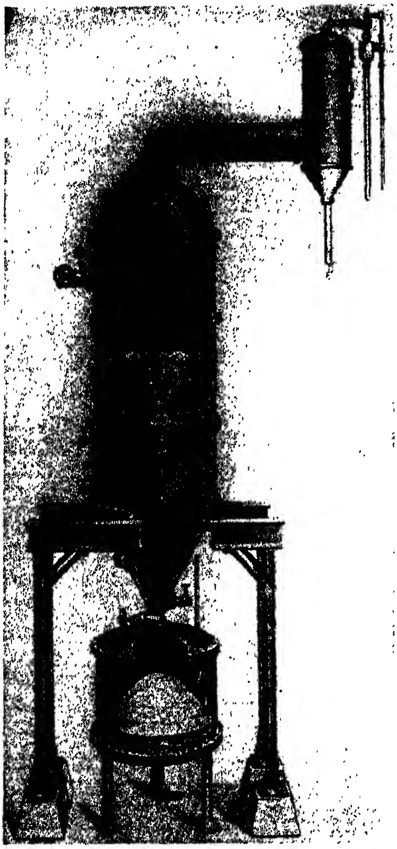

FIG. 8. Vertical Tube Basket Type Evaporator. (Courtesy Swenson Evaporator Co.)

A diagram of the arrangement of the essential equipment for a triple effect evaporator is shown in Figure 9. Live steam, usually exhaust steam from some high pressure operation, is put into the heating element of body I. The vapors arising in the first effect then go to the steam chest of body II and are condensed and removed by a condensate pump. The vapors rising from the second effect in turn go into the steam chest of body III. Then the vapors leaving this last effect are condensed as indicated in the barometric leg condenser.

In this case the second effect acts as the condenser for the vapors from the first effect and the third effect in turn is the condenser for the second effect. Thus it is only necessary to put in one pound of steam to evaporate approximately three pounds of water.

In such an evaporator system the vapor and steam pressures and temperatures will automatically adjust themselves to about the same amount of evaporation in each effect. An ideal distribution might be as follows: temperature of steam entering steam chest for first effect 225° F. (about 4.2 pounds gauge pressure), vapor leaving first effect 195° F. This is steam at a pressure below atmospheric and it is condensed in the steam chest of the second effect which gives off vapor at 165° F. This vapor passes to the steam chest as a third effect which boils the water, giving off vapor at 125° F. which is equivalent to a steam pressure of

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[17] See Chapter 9.

about 26 inches of vacuum. Such a temperature and pressure distribution gives a temperature drop across the fluid films in each effect of about 30° F.

All cases where the pressure of the vapor condensing in the steam chest of an effect is below atmospheric it must be removed by a condensate pump rather than by means of a simple steam trap. It is also necessary that the upper part of the steam chest of each effect shall be connected to a vacuum line in some way so that the non-condensable gases may be removed from each steam chest.

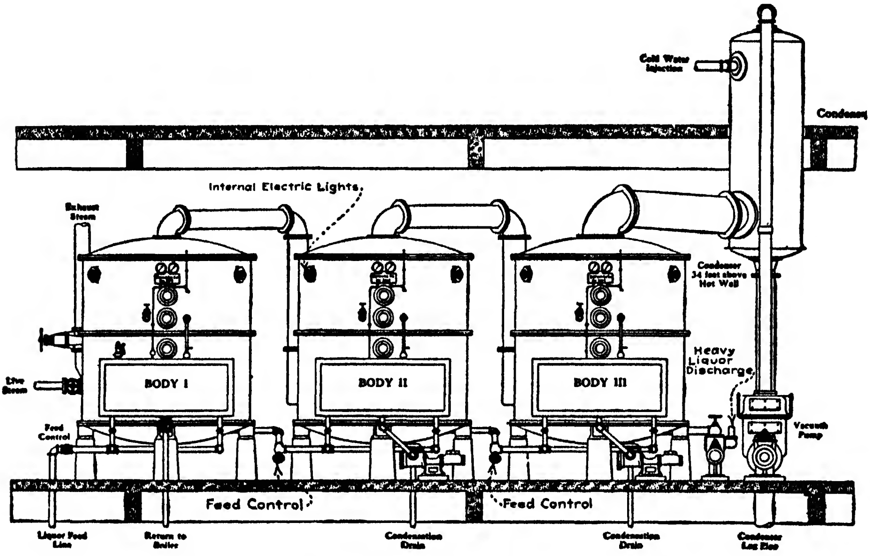

FIG. 9. Diagram of Triple Effect Evaporator.

Characteristics of Multiple Effect Evaporation. There are three important items which are distinctive of multiple effect evaporation.

1. If there were no heat or temperature losses, as many pounds of water would be evaporated per pound of steam used as there are effects. For instance a triple effect evaporator should evaporate three pounds of water per pound of steam used. Actual performance is of the order of 2½ to 2¾ pounds evaporated per pound of steam. This represents a great heat economy.
2. Increasing the number of effects does *not* increase the capacity of the evaporator unit, because the total temperature drop available for heat transfer is the same whether one or a dozen effects are used. For instance, if a single effect evaporator with 100 square feet of heating surface using steam at 5 pounds gauge operating under 26 inches of vacuum evaporates 2000 pounds of water, then three such evaporator bodies, each having 100 square feet of heating surface, connected in series in multiple effect, with the same overall conditions will still evaporate but 2000 pounds of water per hour. Hence, greater steam economy of multiple effect operation is partially counterbalanced by greater equipment cost and maintenance.
3. Since only a portion of the total vapor produced in a multiple effect unit goes to the condenser on the final effect, the amount of cooling water required for a multiple effect evaporator is only a fraction of that required for a single effect evaporator. A single effect uses about 25 pounds of condenser water per pound evaporated but a triple effect requires only 8½ to 9 pounds. Where water costs are high this item may represent a very substantial saving.

This brief discussion covers the most essential features of multiple effect evaporation, but there is a great number of pieces and kinds of accessory equipment which are necessary for the operation of an evaporator plant. The details of such equipment can be studied from some of the items of the Reading List at the end of the chapter and a good deal of information[18] can also be gathered from the descriptive catalogs of equipment manufacturers.

There are many variations in the construction of different types of evaporators some of which are merely minor developments of different manufacturers and others being adaptations to take care of various conditions. Some are designed to eliminate scaling, others are particularly adapted to combat foaming, others are designed to promote very high coefficients of heat transfer and thus get a large capacity evaporator in a small space. But whatever the details of design and construction the principles of operation are essentially as outlined above.

CRYSTALLIZATION

The unit operation of crystallization is very often closely associated with, or is an integral part of evaporation. On the surface it would seem as if the operation of crystallization should be very simple because it is merely that of allowing crystals to form and removing them from the saturated solution of the material in question. However, there are a number of complications which commonly call for a great deal of empirical work, and a good deal of research is necessary before crystallization will be on a truly scientific basis.

The Role of Solubility—Obviously, all crystallization operations must be based upon the solubility of the desired substance in water or whatever solvent is being used. The second important aspect of crystallization is that when material comes out of solution slowly it will almost exclusively crystallize on crystals which are already present, rather than form new ones. A third important factor is that many substances, particularly organic compounds, tend to form strongly super-saturated solutions if no seed crystals are present. The various types of crystallization apparatus are built around these phenomena. Many compounds, particularly inorganic ones such as copper sulfate, are very much more soluble in hot solutions than in cold. If a hot, saturated solution is cooled, crystals will form and can be separated from the mother liquor. Hence, after an initial concentration of the solution, usually by evaporation, the crystallization operation for such materials is primarily one of cooling.

On the other hand, some compounds, such as sodium chloride, are but slightly more soluble in hot solutions than in cold. Hence, cooling is largely ineffective in promoting crystallization. In that case the crystals are formed as an integral part of the evaporation operation[19] by the continuous removal of water from a hot solution maintaining a slightly super-saturated condition. The same method of approach is essentially employed in the crystallization of sugar, though in this case the crystals are formed in a separate evaporator known as the vacuum pan after the principal evaporation has taken place.

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[18] For more of the details of the operation of the multiple effect evaporators in various industries see some of the other chapters in this book, particularly Chapter 9, p. 367, and Chapter 35.

[19] See Figure 8.

The Use of Agitation—As was pointed out above, the formation of crystals is largely by the precipitation of molecules on crystal faces which are already present. This necessarily means that the liquid in the immediate neighborhood of a crystal can become depleted in the soluble material and, for crystallization to proceed, there must be molecular diffusion through the stagnant liquid film surrounding each particle. This indicates that anything which will effectively cut down the thickness of this film will promote rapidity of crystallization. Motion of the liquid past the surfaces has a very marked effect in decreasing film thickness. This indicates that agitation should be an important adjunct in speeding up the formation of crystals. In nearly all modern apparatus, agitation, either by means of paddles or propeller agitators or blowing of air or live steam through the solution is quite widely used. The role of this film resistance around the particles has been carefully studied and the use of agitation is being put progressively on a more scientific basis.[20, 21, 22]

Separating Crystals from Mother Liquor—After crystals are formed they must be separated from the mother liquor. This may be done by settling or filtration or centrifuging operations which will be discussed later. After the mother liquor has been separated from the crystals it is usually returned to the process for further crystallization.

Selective Crystallization and Purification—Almost all crystallization operations, if more than one soluble substance is present, inadvertently involve a process of purification, provided one of the constituents has greater solubility than the other. Obviously the less soluble substance tends to crystallize out first and it is a fortunate feature of this phenomenon that, except in a relatively few cases, the crystals which are formed, tend to be those of a pure substance. A familiar example of this is found in the freezing of sea ice. In that case the crystals which form first upon cooling are those of ice. The remaining salt solution is more concentrated than the original liquor so that a concentrated salt solution is pushed out to the boundaries of the crystals. Eventually the concentration of the solution between the ice crystals becomes so great that the salt crystallizes out, but it tends to be segregated at the crystal boundaries. Hence, if the ice has been formed slowly there will be very large crystals of relatively pure ice surrounded by layers of salt. Advantage has been taken of this by explorers in arctic seas to obtain relatively pure water by melting up large crystals of sea ice.

This phenomenon of the segregation of pure crystals is used industrially in a large number of cases for purification. For instance, in the recovery of potassium chloride from a solution containing many other salts and potassium chloride crystals themselves will be relatively pure. Impure solutions clinging to the crystals after they have been separated can be washed off leaving behind a commercial product of high purity.[23, 24]

Atmospheric Cooling with No Stirring—The time honored method of bringing about crystallization, for those substances which show a large change of solubility with temperature, is to put a hot, saturated solution into an open tank

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[20] Montillon, G. H. and Badger, W. L., Ind. and Eng. Chem. *19,* 809 (1927).

[21] McCabe, W. L., Ind. and Eng. Chem. *21,* 113 (1929).

[22] Wilhelm, W. H., Conklin, L. H. and Sauer, T. C., Ind. and Eng. Chem. *33,* 453 (1941).

[23] Gale, W. A., Ind. and Eng. Chem. *30,* 867 (1938).

[24] Mumford, R. W., Ind. and Eng. Chem. *30,* 872 (1938).

and to allow it to cool. Ordinarily no seed crystals are put into the tank, as a certain number of small crystals will begin to grow as the cooling proceeds after the solution has reached a certain point of super-saturation. After a number of small crystals have been formed, most of the subsequent crystallization will occur by building up on the small crystals.

This type of operation is very slow as, usually, several days are required for complete crystallization to take place in a large tank. A great deal of floor space is required for any operation of substantial magnitude. Also a great deal of hand labor is called for, because the crystals must be shoveled out by hand after the solution is removed. Moreover, the crystals tend to be mixed with any sediment or impurities which settle to the bottom of the tank. Sometimes rods or strings are suspended in the solution from the top, on which crystals will grow. This tends to give large and relatively pure crystals in the upper part of the tank.

The only advantage to this type of operation is that which might be associated with tradition in an old industry and the fact that a relatively small initial investment is required.

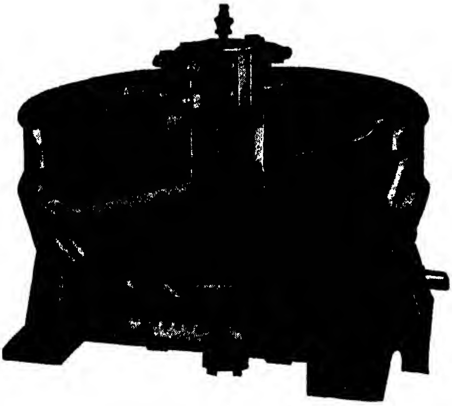

Fig. 10. Water Jacketed Crystallizer Pan.

Agitated Batch Crystallizers—A great improvement on the old batch crystallizer was made with the introduction of the agitated and artificially cooled crystallizer, a simple form of which is shown in Figure 10. A more modern type of batch crystallizer has water circulated through cooling coils, in place of a jacket. The solution is agitated by two propellers operating on a single shaft. The use of cooling water in coils inside the tank, plus the agitation, greatly increases the rate of cooling in accordance with the principles outlined in the previous section on Heat Transfer. Further, the agitation of the solution keeps the crystals in motion which tends to cut down the magnitude of the stagnant liquid film around the crystals through which the molecules must diffuse. This speeds up the rate of crystallization and brings about the growth of more nearly uniform crystals.

The principal drawback of this type of apparatus is that it is still batch equipment and hence its production is small and its upkeep is greater than a corresponding continuous apparatus would be. Another slight drawback is occasioned by the fact that, even with good agitation, the coolest solution will be next to the cooling coils, which tends to bring about a building up of crystals upon those surfaces; which acts like scale on a piece of heat transfer apparatus and cuts down on the rate of cooling. However, this is a much more satisfactory type of apparatus than the old style open tank.

The Swenson-Walker Crystallizer—This type of crystallizer is the most successful and most widely used continuous apparatus in use in the United States. (See Figure 11.) It consists essentially of an open trough with a semi-cylindrical bottom, on which a water jacket is welded, and through which a long slow speed spiral agitator set close to the bottom is running. This agitator not only tends to keep the solution in motion but also feeds the crystals which have been formed out to the end of the apparatus. This crystallizer is usually built up in unit lengths of ten feet and can be made as many units long as desired.

The hot, concentrated solution to be crystallized is fed in at one end of the trough and the cooling water flows in the jackets, usually countercurrent to the motion of the solution. The rate of cooling and of crystal size can be controlled by the temperature and rate of flow of the cooling water as well as the rate of flow of the hot solution. An overflow gate is provided at the end of the crystallizer where the mother liquor and the suspended crystals flow out. The mother liquor is drained off and the wet crystals are raked out to be sent to a centrifuge or other dewatering device.

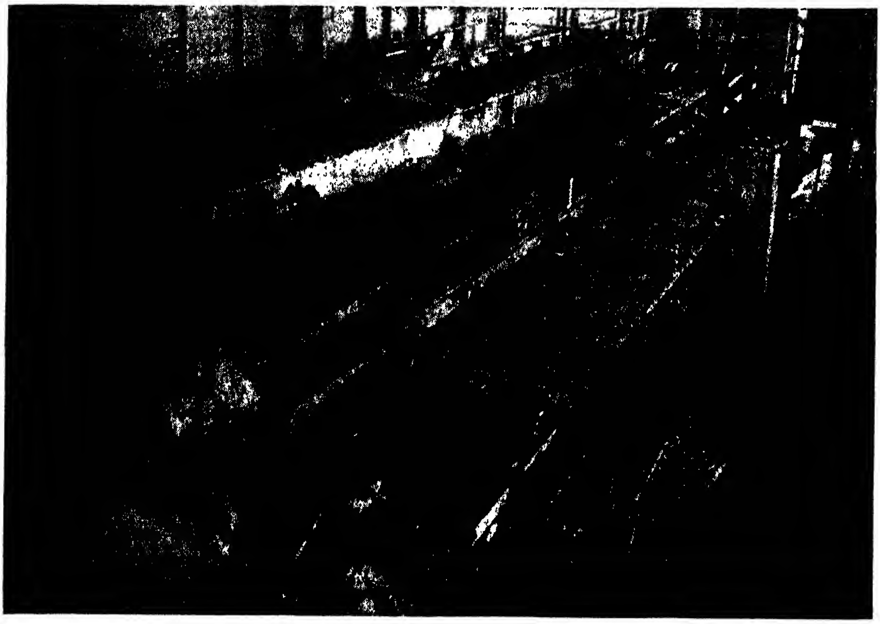

FIG. 11. Swenson-Walker Continuous Crystallizer Handling Tri-sodium-phosphate. (Courtesy Swenson Evaporator Co.)

This type of crystallizer has a very high capacity per square foot of floor space and it requires but very little labor or maintenance costs.

Grainer Pans—All of the crystallizers discussed thus far have been for those types of solutions where the solubility changes markedly with temperature, hence the only operation required to promote crystallization is that of cooling.

In the case of material, such as sodium chloride, which does not change solubility appreciably with temperature, crystallization must be promoted by the continuous evaporation of water. The simplest type of operation for this is essentially an open evaporator known as the grainer. The construction and operation of this is adequately described in another chapter in the book.[25]

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[25] See Chapter 9.

Vacuum Crystallizer—The vacuum crystallizer is another type of apparatus which is used for those substances which do not change solubility appreciably with temperature. It is really a single effect evaporator with provision for handling the crystals which are produced as evaporation proceeds. The principal features of its construction are described in the previous section under evaporators.[26] More of the details and the description of the operation will be found in the chapters on salt,[27] and sugar.[28]

DISTILLATION

As this discussion proceeds, the reader will notice that the majority of the unit operations involve the separation of one substance from another, based on variation in the physical properties of the various chemical compounds involved. Distillation is used for the separation of different compounds which have a sufficiently high pressure to be vaporized at temperatures and pressures which it is feasible to use. Ordinarily, the term is confined to those cases where two or more volatile components are present in a liquid. But it is also common usage to speak of the distillation of water to obtain pure water from a more or less impure solution. That operation is more properly evaporation but usage has completely over-ridden the logic of the names in this case.

Distillation is the most widely used of all of the unit operations in industrial chemistry. Almost all of the billion and a half barrels of petroleum produced annually in this country goes through one or more distillation operations before it appears on the market as a final product. Literally hundreds of different organic compounds are recovered or purified by means of distillation. Going down to low temperature activities, we find that oxygen is largely produced by the liquefaction of air, followed by distillation to separate the oxygen from the nitrogen. At the other end of the scale it is found that such metals as zinc and magnesium are separated from their impurities by means of distillation under low pressure.[29]

The term "distillation" is also usually extended to include the boiling off of the volatile constituents of such solid materials as coal and wood,[30] though the apparatus used in these cases is very different indeed from the distillation apparatus which is used for the separation of those materials which are liquid at ordinary temperatures.

The Role of Vapor Pressure—If a dilute solution of ethyl-alcohol and water is boiled, the vapor rising from the solution will be richer in alcohol than was the liquid. The experimentally determined relationship between the composition of the vapor rising from a boiling solution is shown in Figure 12 where the abscissa is the composition of the liquid in mol per cent and the ordinate is the composition of the vapor in mol per cent. Throughout most the composition range the percentage of alcohol is higher in the vapor than in the liquid. The reason for this is that the alcohol is a more volatile substance than water and hence it has a higher vapor pressure than does water at the same molecular concentration. Thus if a solution of alcohol and water is partially vaporized the

[26] See Figure 8.

[27] See Chapter 9.

[28] See Chapter 35.

[29] See Chapter 24.

[30] See Chapters 14 and 17.

condensed vapors will be considerably more concentrated in alcohol than the original solution.

Batch Distillation Apparatus—It is quite likely that the first use of the operation of distillation was for the making of distilled liquors, an activity which dates very far back indeed. Hence, the first distillation apparatus was probably very simple. Undoubtedly it merely consisted of a vessel closed on top with an outlet leading to some sort of air condenser. Such apparatus is crude but it is essentially the same in principle as the batch distillation apparatus which is in use today.

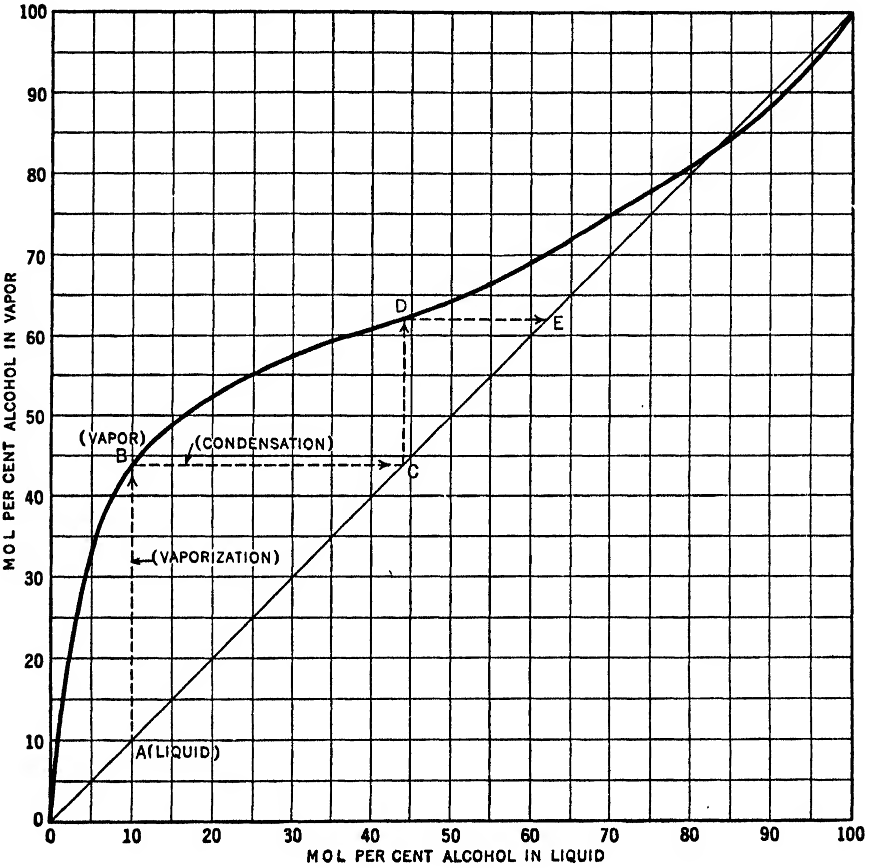

FIG. 12. Equilibrium Diagram for the Distillation of Ethyl Alcohol and Water.

A diagram of a batch vacuum still is shown in Figure 13. The still body, A, contains the liquid to be distilled and it is heated by a steam coil in the bottom. This still pot is surmounted by a vapor bonnet, B, which acts as a baffle to catch any spray that goes up with the vapor. The vapors which pass out go to the water condenser, C, which is most commonly of the shell and tube type with the water on the outside of the tubes and the vapor on the inside. If the still is being operated under a vacuum the condensed vapors would then be caught in the small receiver, D, and pass through the pipe, E, into the vacuum receiver, F. The vacuum is maintained on a system by the vacuum pump, G.

If such a still is to operate at atmospheric pressure, then the vacuum equipment can be dispensed with and the condensed vapors can be discharged into any sort of convenient receiver.

Although a simple still of this type might conceivably be operated continuously, that is a continuous stream of feed into the still pot with a continuous stream of the unvaporized material leaving the bottom, in most cases this would be an impractical procedure because all of the volatile material would not be removed from the liquid in the still pot. Hence, in nearly all cases, such simple stills are operated batchwise. As the distillation proceeds the material in the still pot becomes more and more depleted in the more volatile component. However, it works quite satisfactorily for the separation of the material which has a high vapor pressure compared to the vapor pressures of the materials with which it is associated.

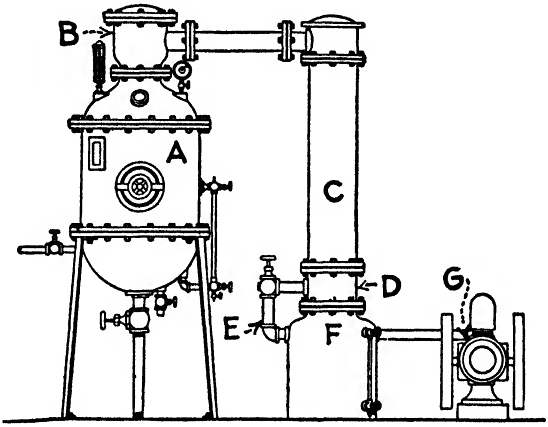

FIG. 13. Vacuum Batch Still.

Rectification—It will be seen from Figure 12 that if a solution containing 10 mol per cent of ethyl alcohol in water (point A) is vaporized, the vapor will contain about 44 mol per cent of alcohol (point B). If this vapor were condensed it would obviously yield a liquid containing 44 mol per cent of alcohol (point C). If this liquid product were again vaporized the composition of the vapor in the second distillation step would be about 62 mol per cent alcohol (point D). This illustrates how it is possible, by means of successive batch distillations, to get higher purity of one of the constituents. Conversely, the material which is not vaporized and is left behind in the still pot is correspondingly enriched in the less volatile constituent.

If there are very great differences in the volatilities of the components of the solution a satisfactory separation may be made by a single step (simple distillation) but for materials having more nearly the same vapor pressures it is necessary to make successive distillation steps as was illustrated in the discussion of the alcohol-water diagram. Obviously it would be advantageous to have an apparatus where the vapor from one distillation unit could be continuously condensed and used as the feed for a second enriching unit. If such an apparatus consisted of a number of still pots, with a vapor line and a condenser for each unit, it would be very cumbersome and would consume a great deal of energy for vaporization and a great deal of cooling water for condensing. However, these successive distillations are very nicely taken care of by means of the rectification columns.

Rectification Columns—In rectification, the vapor from the still pots passes up through a column, the construction of which will be discussed later. Part of the vapor emerging from the top is condensed and sent back through the column as reflux. Such an apparatus, in effect, operates as a number of separate distillation units; one on top of the other. The development of this device represented one of the most important steps in the progress of this particular unit operation.

As was mentioned above, rectification consists of allowing a liquid to flow downwards through a set of contacting units, countercurrent to a stream of vapor flowing upward. The apparatus which is most commonly used for this is the bubble cap column on top of a still pot. Details of one type of such a bubble cap column are shown in Figure 14. Each of the units of this rectifying column consists of a deck, or tray, on which are set a number of bubble caps which are similar to inverted jars with slots cut in the edges. As may be seen by the detailed drawings, the arrangement of liquid overflows for each deck are such that the caps are submerged and the vapor passing up through the column must bubble out through the slots of the cap. This brings it in intimate contact with the liquid so the liquid and vapor tend to come to equilibrium. This necessarily means that, as the two fluid streams progress through the column, the liquid becomes depleted in the more volatile constituents and the vapor becomes enriched. Commonly, the material to be distilled is fed to some plate or deck part way up the column. As the liquid passes downward from this feed plate it becomes less and less rich in the more volatile component and if the apparatus is properly proportioned and operated the liquid will be almost depleted of the more volatile component by the time it reaches the still pot.

Steam coils in a still pot keep a continuous stream of vapor rising up through the column. Part of the vapor which passes out of the top is condensed and returned to the top of the column, as reflux. This keeps the plates full to the overflow level at all times and hence each one of the bubble cap sections in the rectifying column acts essentially as a separate distillation unit.

The part of the column below the feed plate is ordinarily called the "stripping section" because the liquid is there being stripped of its more volatile components. The part above the plate is ordinarily called the "enriching section" because it is there that most of the enriching of the vapor takes place.

If one constituent is much more volatile than any of the other materials in the liquid, the feed may be put in at the top of the column and the whole rectifying section then acts merely as a stripping section. On the other hand, if the material which is to be recovered is not much more volatile than the other constituents then the feed may be very close to the bottom of the rectifying column. The number of decks or bubble cap plates which are required for a given separation depends upon the relative volatility of the constituents which are to be separated, the amount of material which is condensed and sent back as reflux and the efficiency of the bubble cap unit. The relationships between the various variables involved in this apparatus have been worked out very satisfactorily. Their

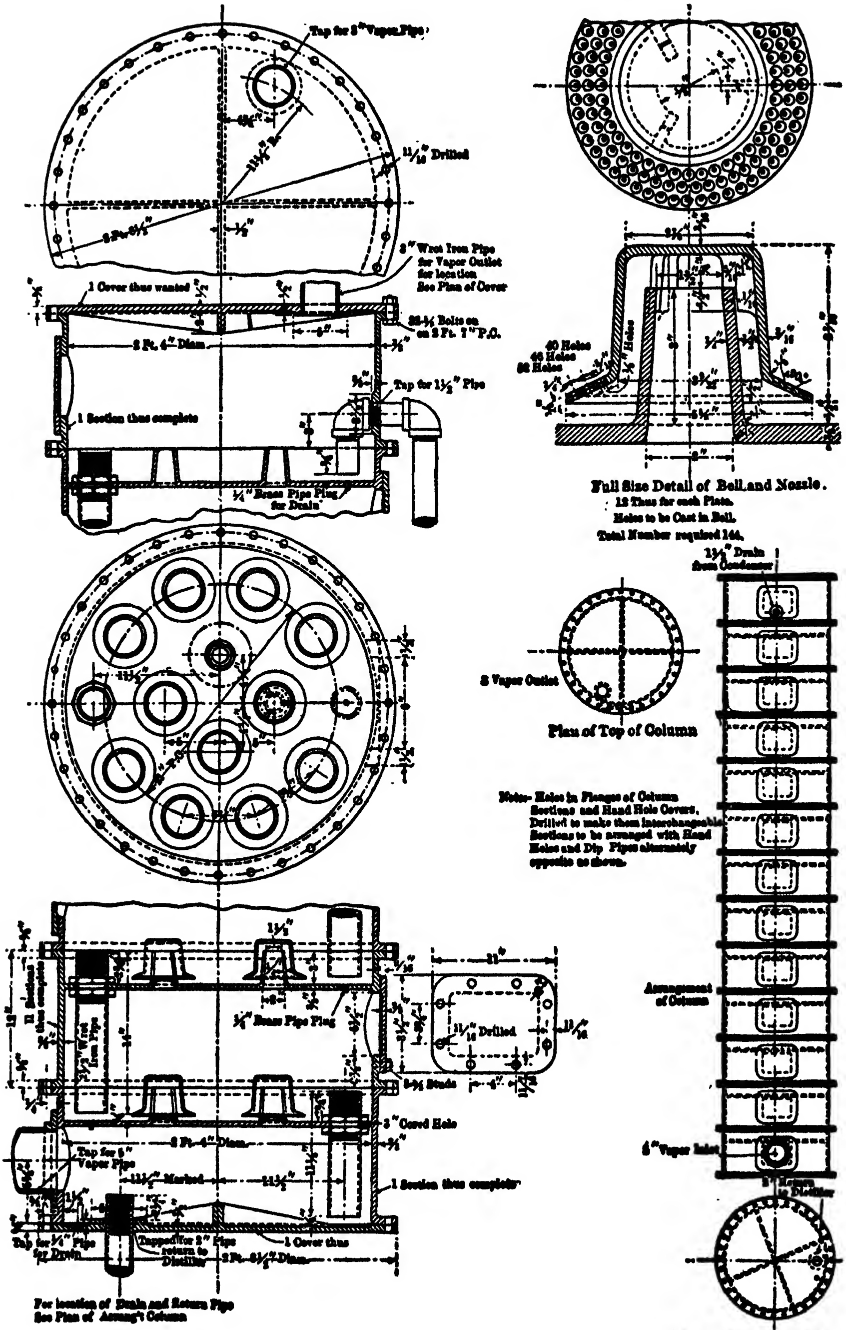

FIG. 14. Cross Section and Details of Bubble Cap Rectifying Column.

treatment is adequately handled in some of the references in the Reading List at the end of the chapter.

Packed Columns—Instead of being equipped with decks of bubble caps the rectification column may be filled with any of various kinds of packing material over which the descending liquid will trickle, affording a large amount of interfacial area. The packing is most commonly some form of short stoneware hollow cylinders (Raschig rings) or of some special shapes such as Berl saddles. This makes a simple and relatively inexpensive but, at the same time, an effective rectification device.

Operation of Rectification Apparatus—The rectification column is most commonly operated continuously; the feed coming in at some intermediate point in the column, the volatile product passing out as vapor at the top, the less volatile constituents leaving the bottom of the still pot. In the petroleum industry[81] it is common practice to take off intermediate products as side streams from the column. However, it is often advisable to provide the column with a large still pot and operate it batchwise. The presence of the rectifying column on the batch still makes it possible to obtain very much sharper separations of the components than is the case if the column is not used.

DRYING

The unit operation of drying is usually considered to consist of the removal of a relatively small amount of water from a solid material by bringing unsaturated air in contact with it. This definition is by no means rigid or all-inclusive but it will cover most of the material discussed in this section.

Drying Theory—When a wet surface, whether it be pure water or merely a moist solid, is dried by an air stream, molecules of water vapor must move out from the liquid surface into the air and heat must move in to the liquid to supply the heat of vaporization. Obviously, then, drying involves both mass transfer and heat transfer between a gas and a liquid (or solid) phase. As in all such operations an inert gas film is present next the phase boundary, offering resistance to the transfer of both heat energy and water molecules. The film concept necessarily plays an important part in the theory of drying.

If a solid with a very wet surface is held in an air stream of constant temperature and constant humidity, then the *rate* of moisture removal will be constant for a considerable time until the surface becomes relatively dry. This is, not unexpectedly, called the "constant rate period" and it holds during that time when the solid surface is so wet that it presents practically a continuous sheet of water to the air stream. During this period, practically all the resistance to transfer is in the surface film of air. Hence, increased air velocity markedly increases the rate of drying, since it cuts down the thickness of the surface film. The rate of drying is also approximately directly proportional to the difference between the humidity (measured in pounds of moisture per pound of bone dry air) in the saturated air at the interface and the humidity in the main body of the air stream.

After the surface of such a solid material has become relatively dry, the

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[81] See Chapter 14.

moisture must diffuse from the inside of the piece out to the surface. This is a relatively slow process, so as drying proceeds beyond the constant rate period, the rate falls off, going into what is commonly known as the "falling rate period." In general, it is approximately true that the time required to transfer a given amount of moisture through a solid by diffusion is proportional to the square of the thickness of the piece. It is obvious, then, that there is a distinct advantage in keeping the solid pieces to be dried as thin as possible. On the other hand, increased air velocity has relatively little effect on the rate of drying during the falling rate period.

Equilibrium Moisture—Solid material of given moisture content exerts a definite water vapor pressure. This relation between the moisture content and its equilibrium water vapor pressure can be determined only by experiment. This equilibrium water vapor pressure naturally increases with temperature.

Important Variables in Drying—The foregoing discussion of the theory indicates that to promote the most rapid drying it is necessary to have: (1) a rapid movement of air past the solid, particularly during the constant rate period, (2) low humidity in the drying air, (3) high temperature, and (4) the solid material in pieces of thin cross-section, to diminish the length of the falling rate period. For practical reasons, a balance is usually struck between these various factors to give the best performance within economical limits.

One factor of importance, particularly with organic materials, is often the limiting temperature to which a material may be heated without injury. If the solid is easily injured by heat it is often advantageous to resort to drying under a vacuum, at relatively low temperatures. The reduction of pressure diminishes the back pressure of water vapor in the air stream and thus speeds up the drying operation.

Classification of Drying Apparatus—Any rigid classification of drying apparatus is impossible, largely because the equipment has evolved along empirical lines without a common background and has followed no uniform pattern. However, one type of classification, based on the [32] form of the material to be handled, gives a fairly cleancut picture. The important points of this classification are shown in Table 2.

It will be noticed that class V in Table 2 does not fit in exactly with the definition of drying as given at the beginning of this section, since no solid phase is present at the beginning of the operation. However, a solid phase is present before the operation is complete so it can logically be classed as drying.

Equipment for Drying Continuous Sheets—The equipment for this type of drying has been brought to its highest state of perfection in the paper industry. It is amply illustrated in another chapter.[33] The paper is passed over rapidly rotating rolls, which are internally heated with steam. In this case, the operation is concerned almost entirely with raising the temperature of the stock, and practically not at all with controlling the air stream which removes the water. The speed of travel of the paper through the machine is sufficiently high to cut down the thickness of the air film on the surface to a very low figure. Natural circulation in the vicinity of the machines is sufficient to carry off the water vapor.

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[32] "Modern Drying Machines," Ernest Bern, London (1926).
[33] See Chapter 37.

This is an extremely rapid type of drying as it is completed in a matter of seconds rather than hours or days required for some other materials. Such speed is possible only because thin sheets can be heated very rapidly.

Dryers for Granular or Loose Material—The simplest form of dryer for this class of material is an adaptation of the rotary kiln. Such a dryer consists of a revolving shell into which the material is fed. See Figure 15. Hot air or hot flue gases are mechanically circulated through the dryer. It is built in a direct heat and indirect heat types. In the former, air, mixed with the products of combustion, is used as the heating medium. In the indirect heat type, the air is heated either by a steam coil or by passing through a heater in which the products of combustion do not come in contact with the air. Higher operating temperatures and greater capacities are obtainable where the material is suited to this type of drying. The shell can be constructed of any suitable material.

TABLE 2—CLASSIFICATION OF DRYING EQUIPMENT

Material to Be Dried	*Type of Dryer Equipment Commonly Used*
I. Continuous sheets, e.g. paper.	Rotating cylinders, material outside cylinders.
II. Granular or loose.	(a) Rotary—material inside rotating cylinder. (b) Continuous moving mesh belt in tunnel.
III. Cut sheets or masses placed on conveyors or trays.	(a) Batch. (1) Atmospheric. (2) Vacuum. (b) Continuous. (1) Tunnel.
IV. Pastes or sludges.	(a) Agitated driers. (1) Atmospheric. (2) Vacuum.
V. Materials in suspension or solution.	(a) Rotating drums. (1) Atmospheric. (2) Vacuum. (b) Spray driers. (1) Air. (2) Superheated steam.

Contact between the air and granular material is sometimes improved by internal spiral agitators (see Figure 16) or by flanges welded to the inside of the shell.

This type of dryer is usable for such diverse materials as aluminum hydrate, ammonium sulfate, corn germ, lime, sewage sludge, tobacco stems, and zinc oxide. It is not satisfactory for very fine dusty materials such as starch. In such cases it is necessary to use some form of tray dryer where there is no agitation of the solid and where air velocities are low.

For relatively coarse granular material, tunnel dryers which carry the solid through continuously on wire mesh belts are sometimes used. This makes it possible to send the drying air not only over, but through, the bed, thus affording intimate contact and rapid drying.

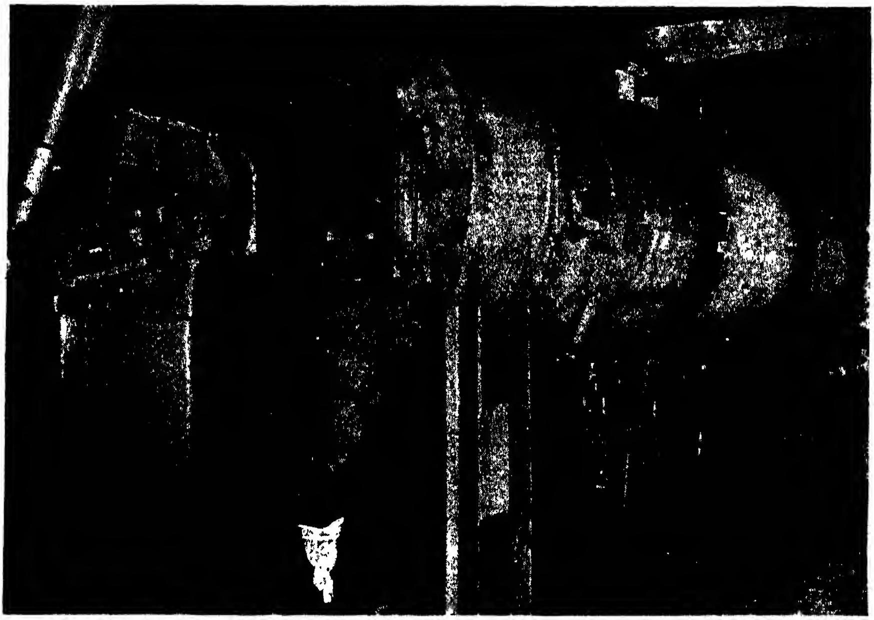

FIG. 15. Rotary Dryer with Vibratory Feeder. (Courtesy Blaw-Knox Co.)

FIG. 16. Spiral Agitator for Rotary Dryer. (Courtesy Buffalo Foundry and Machine Co.)

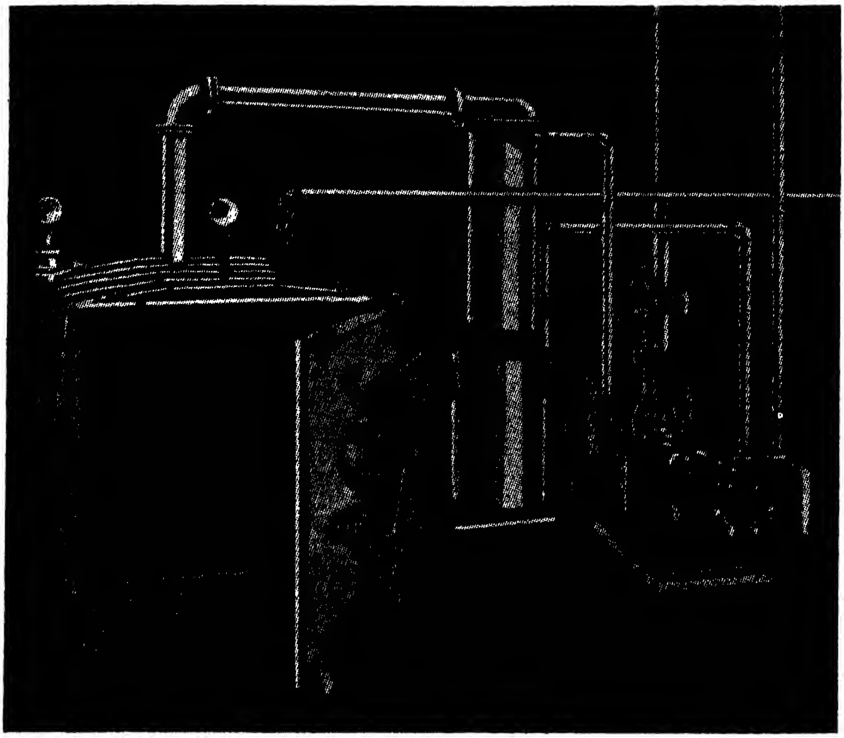

FIG. 17. Vacuum Shelf Dryer.

FIG. 18. Tunnel Tray Dryer. (Courtesy Proctor and Schwartz, Inc.)

Dryers for Materials on Trays—For batch operations, this dryer consists merely of a closed compartment in which the material is placed on trays and warm or hot air circulated.

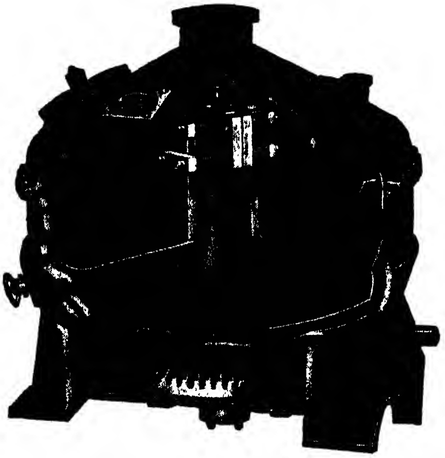

FIG. 19. Vacuum Pan Dryer. (Courtesy Buffalo Foundry and Machine Co.)

In many cases, particularly for organic materials injured by high temperatures, it is advantageous to dry under a vacuum. Such apparatus usually consists of a heavy vacuum compartment with shelves consisting of steam jackets, the entire enclosure being attached to a dry vacuum pump. See Figure 17.

Tunnel Dryer—For the drying of pigments, textiles, leather, glue, and many other materials, the tunnel dryer is employed. The length of the tunnel depends upon the material to be dried and it may be from 20 to 100 feet or more in length. The material to be dried is placed on racks, shelves, bars, or hooks, which, by mechanical means, are caused to pass slowly through the drying chamber. In tunnel drying, it is usually the practice to introduce the goods at the cool end and deliver at the hot end of the tunnel. See Figure 18. Such tunnel dryers are also sometimes adapted to vacuum operations.

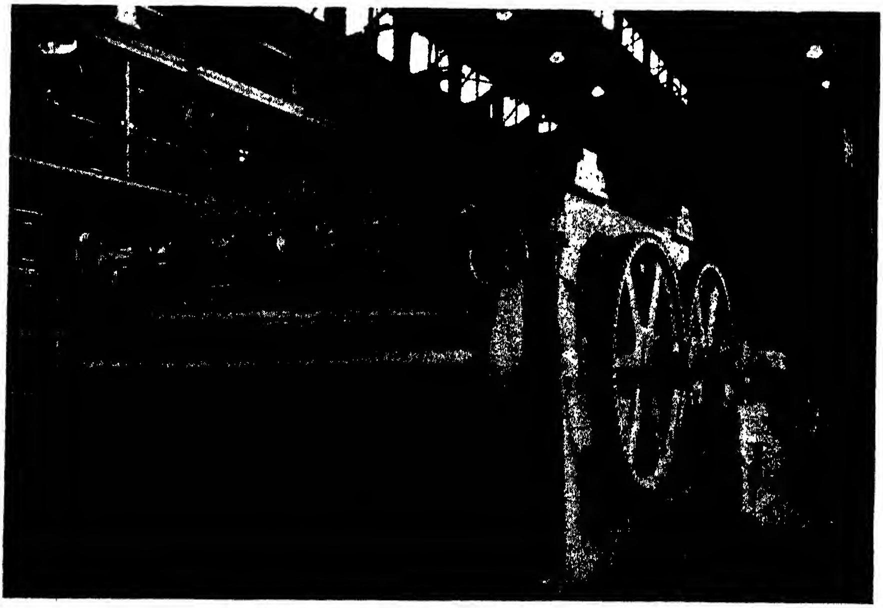

FIG. 20. Atmospheric Double Drum Dryer. (Courtesy Buffalo Foundry and Machine Co.)

Dryers for Pastes or Sludges—For drying sticky pastes or sludges or granular material, some sort of agitated pan dryer, where heat is supplied by a steam jacket, is commonly used. See Figure 19. If the vessel is completely enclosed it can be operated under a vacuum.

The particular virtue of this type of apparatus is that the agitation keeps breaking up the solid material, exposing new surfaces, thus accelerating the drying operation. It is suited for handling comparatively small batches of materials or for combining a number of operations in succession, such as heating, cooling, distilling under reflux, evaporating, extracting and drying, without having to transfer the material. The cover is provided with observation glasses, vapor connections, and charging doors. A discharge door is conveniently located at the side of the dryer. An extension ring can be placed between the body and the cover to increase the holding capacity. Arms can be added to the agitator to break up the material and prevent lumping.

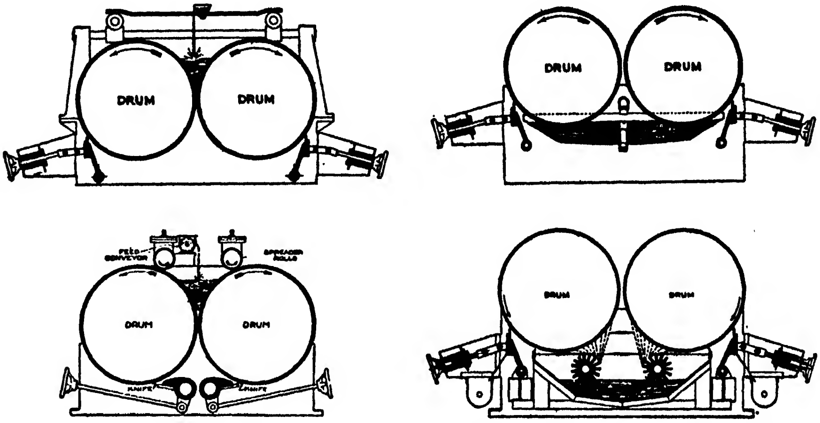

FIG. 21. Types of Feed Used for Drum Dryers. (Courtesy Buffalo Foundry and Machine Co.)

Such an apparatus can be operated at atmospheric pressure or under vacuum. Similar apparatus is available without the enclosed tops, for atmospheric drying.

Dryers for Materials in Suspension or Solution—Drum drying is an economical and continuous method for producing dry materials at low operating cost, directly from liquids containing solids in solution or suspension. This process is applicable to a wide variety of materials including chemicals, dyes, pharmaceuticals, and food products.

The process of drum drying consists of applying the liquid material to a revolving heated drum, where the moisture is quickly evaporated during a partial revolution. Then the dry material is removed by a stationary knife. This basic operation principle is used with various modifications on all types of drum dryers. To successfully meet these widely differing requirements, dryers are built for vacuum and atmospheric operations; in single, double drum, twin drum, and multiple stage types. An atmospheric double drum dryer is shown in Figure 20.

The principal difficulties attending the development of this type of dryer were concerned with feeding arrangements. It was found to be necessary to use different types of feeds for different materials, depending on the viscosity, specific gravity, and such characteristics as the stickiness of the partially dried material. These different types of feeder mechanisms which have been developed are shown in Figure 21.

Such drum dryers are readily adaptable to vacuum operation, if adequate apparatus is provided for continuously maintaining feed and dried product removal. A diagram of such a typical apparatus is shown in Figure 22.

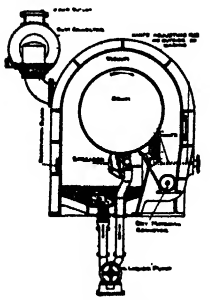

FIG. 22. Cross Section of Vacuum Drum Dryer. (Courtesy Buffalo Foundry and Machine Co.)

Spray Dryers—One way of promoting rapid drying of materials in solution or suspension is to spray it, in fine droplets, into a stream of hot air or flue gas. Such dryers are used more or less extensively abroad but only to a limited extent in the United States.

The solution to be dried is sprayed into a chamber, through a nozzle, or by depositing it on a rapidly rotating disk. Hot air or flue gases are sent through the apparatus, either in countercurrent or cross flow to the stream of droplets. The material dries very quickly in the form of small pellets or powder. The finer particles are carried out with the exit gas and caught in a dust catcher. The larger ones fall to the bottom of the apparatus and must be removed by a mechanical discharge arrangement.

The principal difficulties in construction and operation are found in preventing the droplets from arriving at the walls of the chamber in a partially dried condition. If they are not completely dried by the time they come to the wall, the product adheres as a sticky, partly dried coating.

For materials that are not injured by heat, such a dryer can be directly fired, thus promoting high capacity. For organic materials which are easily injured, such as soap, or more especially milk, warm air must be used as the drying medium.

AIR CONDITIONING

Air conditioning is a term of rather loose definition but, in general, it is taken to mean the simultaneous control of the temperature and the humidity of air to some prescribed values. The largest application in recent years has been found in the improvements of comfort conditions, particularly in summer, for offices, stores, factories, and residences. However, the control of both humidity and temperature is having increasing importance in various manufacturing processes. For instance, there is a great advantage in maintaining the proper humidity in many of the textile spinning and weaving operations. Formerly, where such conditions were highly desirable it was customary to have the plant located in areas where the humidity was approximately that desired, but in more recent times the practice is sometimes followed of conditioning the factories in which the work is taking place. Much of the work in plastics and surface coatings calls for control of humidity to some more or less constant figure. One of the largest scale operations now in the process of development is that of reducing the humidity or amount of water vapor going into the air blown into iron blast furnaces. This makes for smoother and more efficient operation.

Principles of Air Conditioning—Air conditioning is a combination of two other unit operations: the heating or cooling of air by the usual heat transfer methods, plus the mass transfer of water vapor to or from the air stream. The principles of air conditioning are really quite simple but the complications which arise from the possible peculiar combination of these two operations have led to much confusion in the knowledge and understanding of air conditioning practice.

If air and water are left in intimate contact at some particular temperature then the air becomes saturated with water vapor. The temperature at which the air becomes saturated is known as the "dew-point." If a sample of air which is initially partially saturated with water is cooled below the dew-point, water will condense out, thus going through the operation of dehumidification. On the other hand, if partially saturated air is brought in contact with water which is above the dew-point temperature then this contact results in adding humidity to the air. These relations involving temperature and humidity are conveniently summarized in the form of humidity charts.[34]

A second well-known means of reducing the humidity in air is to allow it to be in contact with hygroscopic salts such as calcium chloride. As the vapor pressure of water over such salts or other strong solutions is very low, the water vapor obviously must move from the air to the surface of the salt, or the solution.

A third well-known way of reducing the humidity in air is by bringing it in contact with an adsorbent such as silica gel or alumina gel. These act very similarly to the hygroscopic salts such as calcium chloride, except that, in this case, the adsorption is a purely physical phenomenon, rather than the formation of a hydrate as is the case with calcium chloride.

As far as quantitative considerations are concerned, the most important thing to be remembered in operations of humidification and dehumidification is that water has a high latent heat of vaporization and no matter what method is used for adding or subtracting water from air, this latent heat is still operative. Whenever air is dehumidified about one thousand B.T.U. are liberated for each pound of water vapor removed; and if air is humidified about one thousand B.T.U. are absorbed for each pound of water vapor put into the air. Thus dehumidification tends to raise air temperature and humidification tends to lower it.

Use of Direct Contact with Water—Particularly in arid country, air can be easily and effectively cooled by bringing it in contact with a water spray or a surface which is kept moist. Thus if air at 100° F., 20 per cent saturated with moisture, is brought in contact with water at 70° F. the humidity of the air will increase but it will be quite markedly cooled. This is quite largely used as a means of air conditioning homes and factories in the southwest United States. On the other hand, if air at 100° F. and 90 per cent saturated comes in contact with water at 70° F. there is a slight dehumidification of the air and but little if any cooling, unless a very large quantity of water is used.

Where air humidities are relatively low, this operation affords a means of cooling water very effectively for industrial purposes. Thus, if hot water is brought in contact with relatively dry air, both the water and the air are cooled by the latent heat of vaporization. This is the principle of the operation of spray

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[34] Badger, W. L. and McCabe, W. L., "Elements of Chemical Engineering," 2nd ed., p. 661, McGraw-Hill Book Co. (1936).

towers or atmospheric cooling towers. See Figure 23. Such devices are widely used for the cooling of condenser water from power plants as well as for bringing down the temperature of water used in chemical processes, particularly in the arid countries. This operation is not air conditioning but it operates on the same principles.

Obviously, by controlling water temperatures and flows in a spray tower or similar apparatus, it is possible to add humidity to the air rather than subtract it. Hence, a spray tower, or similar apparatus can be used for humidifying atmospheres where that is desirable, by simply adjusting conditions.

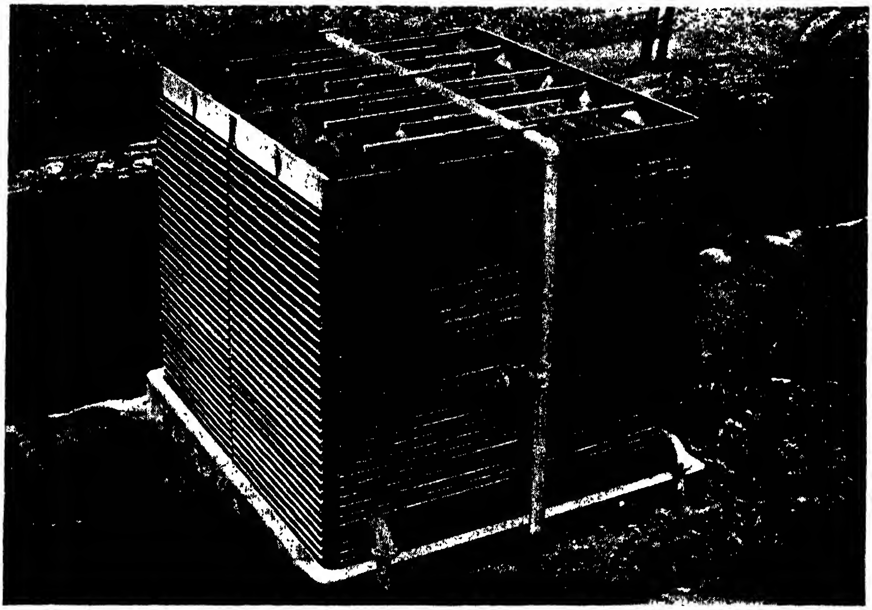

Fig. 23. Atmospheric Cooling Tower. (Courtesy Marley Co.)

Use of Refrigeration—If a large quantity of cold water is available, it is quite simple to dehumidify air by bringing it in contact with this water. A more common method is to pass the cold water inside the metal tubes arranged in banks over which the air is blown. In this case the heat passes from the moist air into the water through the metal wall. As soon as the air has been cooled to the dew-point, water condenses on the surface of the coils, thus dehumidifying the air. However, large quantities of cold water are usually not available so, ordinarily, means must be used for artificial cooling. Some type of mechanical refrigeration plant is usually used. Another more or less common method is to evaporate a portion of the recirculated water under a high vacuum. In such an apparatus the latent heat of vaporization quickly cools the water but the apparatus must operate under the vacuum which is equivalent to the equilibrium vapor pressure of water at the desired temperature. For instance, water at 45° F. only has a vapor pressure of 7.6 millimeters, which calls for quite low pressure evaporation. The maintenance of vacuums of this order is usually accomplished by steam-jet ejectors.

Use of Adsorbents—The use of adsorbents such as silica or alumina gel is another method used for the dehumidification of air. The adsorption capacity of these materials for water is quite high, hence a relatively small volume of the bed may be used for treating large quantities of air.

It is necessary to have two or more beds of this material, operated batchwise. After the bed becomes saturated with moisture it must be dehydrated by heating to a high temperature, usually by means of flue gases. Then it is ready to go through the adsorption cycle again.

In this kind of a system, since the solid alumina or silica gel offers no means of cooling, the temperature of the air will rise as it is dehumidified because of the release of the latent heat of condensation. So, if it is desired to have both cool and dehumidified air, it is necessary to institute some sort of cooling arrangement using either cold water or refrigeration.

Use of Hygroscopic Salts—Similar action may be obtained by passing air over or through beds of material such as calcium chloride which readily absorb water of hydration even from air of quite low humidity. As the salt becomes hydrated it first forms the usual dihydrate $CaCl_2 \cdot 2H_2O$ but it continues to absorb moisture until it drips away as a strong solution of calcium chloride. This offers a means of dehumidifying air with a low equipment cost installation, although the maintenance cost of supplying calcium chloride without reuse is rather high.

The next obvious step along this line, which is now being more widely used, is to dehumidify air by bringing it in intimate contact either with sprays or surfaces moistened with strong solutions of a hygroscopic salt such as calcium chloride. This will pick up moisture from the air, and the water condensed dilutes the solution. This solution can then be concentrated by means of simple atmospheric evaporators and the reconcentrated solution sent back into the dehumidification cycle. In this case, as in that of the adsorbents, it is necessary to cool the air after it has been dehumidified, if it is desired to have both cool and dry air.

In these operations of air conditioning it is obvious that there is a transfer of heat as well as materials between two phases, hence the film concept previously outlined is entirely applicable. The correlation of information on the basis of film coefficients of heat and material transfer has been of paramount importance in the design and operation of the modern air conditioning equipment. The engineering principles upon which these designs are based can be found in some of the references at the end of this chapter.

GAS ABSORPTION AND DESORPTION

The unit operation of gas absorption usually refers to the dissolving of a gas in a liquid. This operation is very widely used for the recovery of various materials. For instance, in the absorption of sulfur trioxide, SO_3, in sulfuric acid[35] to make stronger sulfuric acid or the absorption of nitric oxide in water for the

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[35] See Chapter 7.

production of nitric acid[36] or the absorption of carbon dioxide, CO_2, from flue gases in ethanol amines for the making of solid carbon dioxide. These materials which have just been mentioned are gases at ordinary temperatures and pressures but the operation of gas absorption also applies to the recovery of vapors from dilute gaseous solutions. For instance, benzene, toluene, and xylene are recovered from manufactured gas[37] by absorbing them in a non-volatile "wash oil." A very similar operation is involved in the production of natural or casing head gasoline by the absorption of such hydro-carbon constituents as propane and butane from "wet" natural gas for the production of gasoline. Gas absorption is also frequently used for a straight purification operation such as the removal of odors from certain organic vapors. Another large scale application of purification by gas absorption is found in the preparation of gaseous reactants for the making of synthetic methanol.[38] In this case carbon dioxide, CO_2, carbon monoxide, CO, and hydrogen, H_2, come from the gas producers as a mixture. Before the synthesis of methanol it is necessary to remove the CO_2 from the other gases. Carbon dioxide is much more soluble in water than either CO or H_2 so that purification is usually carried out by passing the gases through an absorption tower, countercurrent to a stream of water under high pressure. The CO_2 is absorbed while the other gases pass on through, with practically all the CO_2 removed.

Desorption or Stripping—The opposite of absorption is desorption, or the removal of gases from solutions. An example of this is found in connection with small units for the oxidation of ammonia to produce nitric oxides.[39] The source of ammonia is often aqua ammonia. This solution is passed down a tower countercurrent to a stream of air passing upward. The air stream desorbs, or strips, the ammonia from the solution. A large-scale example of desorption is found in modern manufactured gas[40] plants. Hydrogen sulfide is removed from gas by sodium carbonate solution. This solution containing H_2S in loose chemical combination is passed down a tower through which air is blown. The air stream desorbs, or strips out, the H_2S.

In practically all cases where absorption is employed, some desorption operation follows, so the absorbing liquid may be re-used. However, this frequently employs high temperatures and often is more of a distillation operation than a mere reversal of absorption.

Films in Gas Absorption—The film theory previously discussed is completely applicable to the operation of gas absorption or desorption. In this case, there are two fluids involved so it is logical to assume that there are two inert films, one on the gas side of the interface and one on the liquid side. The application of this two-film theory[41] to gas absorption represented a great step forward, in quantitative applications. The major resistance to transfer of gas into a liquid may reside in the gas film or in the liquid film, depending to a considerable extent upon the solubility of the gas. For instance, a highly soluble gas like ammonia, when it once gets to the liquid interface, will readily dissolve, so there is relatively little resistance in the liquid film. Most of the resistance in the absorption of ammonia from an air stream will be in the gas film. On the other

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[36] See Chapter 8.

[37] See Chapter 15.

[38] See Chapter 4.

[39] See Chapter 8

[40] See Chapter 15.

[41] Whitman, W. G., Chem. and Met. Eng. 29, 147 (1923).

hand, a very insoluble gas, such as oxygen, will have most of the resistance in the liquid film.

Apparatus for Gas Absorption—As is the case in nearly all the unit operations, the apparatus must be adapted to provide a maximum of intimate contact between two phases. The apparatus most commonly used for this is a simple tower which is filled with some sort of packing to afford a large amount of contact surface. These packings may be wooden grids, stoneware rings, coke, stone, or steel turnings, or any of a variety of special stoneware shapes which are used to provide a maximum of surface. In all cases the liquid which is the absorbent passes down the tower and the gas passes countercurrently upward.

In some cases it has been found advantageous to use bubble cap towers such as are more commonly employed in distillation. In some cases, for very soluble gases such as ammonia in sulfuric acid for the recovery of ammonium sulfate in gas works, it is only necessary to have a large bubbler where the gas bubbles through a layer of sulfuric acid.

FIG. 24. Unassembled Parts of Chemical Stoneware HCL Absorption Tower. (Courtesy Maurice A. Knight Co.)

In cases where there are very high heats of absorption, special apparatus must be used. The outstanding example of this is found in the absorption of HCl in water for the production of hydrochloric acid.[42] The heat of absorption in this case is so great that a large amount of cooling surface must be provided. This is accomplished by passing the gas in a small stream over practically stationary water surfaces. The gas-liquid contact is not very extensive, so the rate of absorption is cut down and the heat dissipation is taken care of by natural convection and radiation from the apparatus. The equipment usually consists of horizontal fused quartz or stoneware vessels, arranged in series so the liquid slowly cascades from one to another. Elongated S-bends are often used or, perhaps more commonly, special shapes known as "tourills." More recently, the absorption of HCl has been successfully carried out in packed stoneware towers containing a series of perforated plates with a stoneware cooling coil provided at each plate. (See Figure 24.) The necessity for water cooling is obvious if one considers the fact that the solubility of HCl decreases very markedly with increase in temperature, so in order to get concentrated solutions it is necessary to keep the temperature of the liquid down.

The use of the corrosion-resistant metal tantalum results in high coefficients

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[42] See Chapter 9.

of heat transfer and has resulted in the use of specially designed, compact HCl absorbers of high capacity.[42a]

Adsorption—A related operation is that of gas adsorption, where the gas is adsorbed on or in a solid material. This is widely used in volatile solvent recovery from air streams, such as is found in printing establishments and for the recovery of solvents from plastics, rubber, and dry cleaning industries. In those cases a relatively small percentage of organic vapor passes out with an air stream. It is passed through a bed of activated carbon[43] which readily absorbs the organic vapors, allowing the air to pass through. (See Figure 25.)

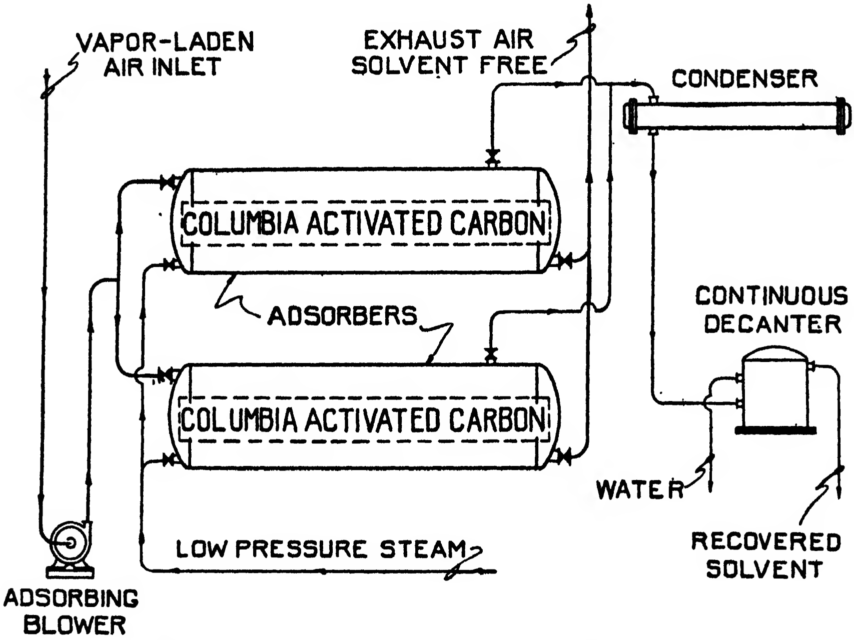

Fig. 25. Diagram of an Activated Carbon Solvent Recovery System. (Courtesy Carbide and Carbon Chemicals Corp.)

This is a batch apparatus and at least two units must be used, for after the activated carbon has become saturated with the organic vapors it must be taken off the line and the organic vapors removed, usually by passing steam through the bed. This removes the vapors and the mixture of condensed steam and organic vapors is usually distilled so that the solvent can be used over in the process. After the bed has been thoroughly activated in this way, it can be put back on the line for re-use in the absorption cycle.

EXTRACTION

Extraction might be described as the operation wherein the soluble constituent is removed from a solid or a liquid by the use of a solvent, which, in a great many

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[42a] See Chapter 9, p. 378. See also Hunter, F. L., Trans. Amer. Inst. Chem. Engrs., 37, 741 (1941).

[43] See Chapter 18.

cases, is water. The most commonly observed example of this operation is the making of coffee by pouring hot water through a granular bed of ground coffee, in the common percolator. The soluble materials are rapidly extracted from the surface and interior of the pieces of the coffee bean. A similar apparatus is used industrially for making coffee extracts. (See Figure 26.) A large scale example of this type of extraction can be found in the beet sugar industry, in the diffusion battery. The operation of the diffusion battery is quite completely described elsewhere.[44] The equipment is so arranged that the operation proceeds in a semi-continuous fashion, the percolation of solution through each bed of the shredded beets going continuously until the bed is exhausted. But the removal of the solid material is a discontinuous operation.

Returning to the analogy of making coffee, the older and perhaps more widely used method is that of boiling coffee and then pouring off the liquid at the desired time. This would be the operation of extraction followed by decantation and is still very widely used, particularly for small batches of material. It is applied in the making of logwood extracts for dyeing and tanning extracts and in a large number of places in the pharmaceutical industry.[45]

FIG. 26. Jacketed Coffee Extractor. (Courtesy Blaw-Knox Co.)

Extraction from Sludges—If the solid material from which material is to be dissolved, or extracted, is in the form of a finely divided sludge, then the operation is somewhat more complicated, but it offers the opportunity for truly continuous operation, for a sludge is a more or less viscous fluid and can be pumped. For the extraction of this type of solid, ingenious devices for affording good contact between solids and liquids, as well as opportunity for settling and hence separation, have been devised. The most common of this type of apparatus is the Dorr Thickener. A diagram is shown in Figure 27. In this apparatus the sludge is sent in at a central downtake and agitators keep the material stirred up and in intimate contact with wash water which is fed in with the sludge. The sludge slowly settles to the bottom and is taken out by means of a sludge pump. The wash water, which has removed the soluble materials, slowly flows to the edge and out through an overflow trough. In order to remove completely all of the soluble material and to concentrate it as much as possible, this apparatus is usually arranged countercurrently in multi-stage, that is, the wash water from the first unit will go for extraction of still further material from the solid in the

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[44] See Chapter 35.
[45] See Chapter 34.

second unit and so forth. This arrangement of apparatus is shown by the flowsheet for the aluminum sulfate manufacture shown in Figure 28.

Another widely used application of this is the making of caustic soda from lime and soda ash wherein calcium carbonate is precipitated and sodium hydroxide washed from the sludge.[46] Various modifications and adaptations have been worked out for liquid-solid extractions, but they all operate on the essential principles as outlined above.

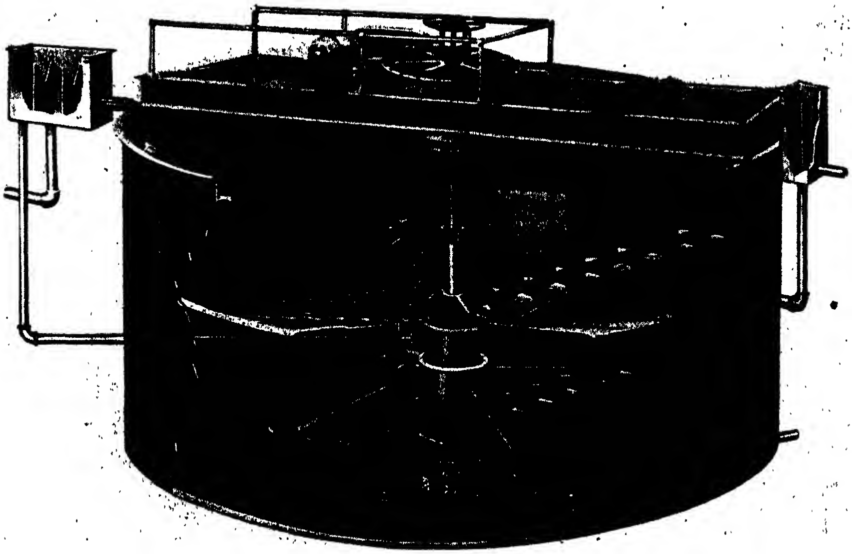

FIG. 27. Dorr Thickener. (Courtesy Dorr Co.)

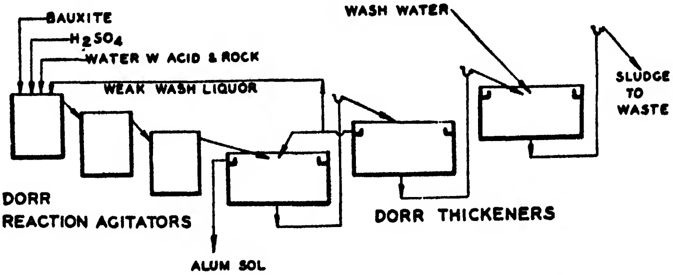

FIG. 28. Flow Diagram for Aluminum Plant. (Courtesy Dorr Co.)

Liquid-Liquid Extraction—Another type of extraction is liquid-liquid extraction, sometimes called solvent extraction. This operation is illustrated by a common experiment of physical chemistry showing the distribution ratio of certain materials between solvents. If bromine water is brought in contact with chloroform and thoroughly shaken, two liquid layers will separate and, by observa-

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[46] See Chapter 10.

tion of color, it can be seen that a large part of the bromine has left the water and gone into the chloroform layer. This is a simple case of liquid-liquid extraction. It is based on the transfer of a soluble substance from one liquid to another, the two liquids being mutually insoluble.

Applications of Liquid-Liquid Extraction—This type of extraction has a number of applications. For instance, acetic acid from wood distillation[47] is sometimes removed from water solution by extraction with ether or isopropyl ether. This concentration can be effective despite the fact that acetic acid is completely soluble in water. Acetic acid so removed from a water layer and dissolved in an organic liquid must then be recovered, usually by a distillation process. The manufacture of aniline from nitrobenzene produces a quantity of water which contains a few per cent of aniline. This aniline is often recovered by liquid-liquid extraction with nitrobenzene.[48]

Probably the largest scale operation of extraction at the present time is found in the refining of petroleum products, particularly lubricating oils. It has been found that some organic materials have a greater affinity for some of the undesirable compounds in lubricating oil stock, hence, countercurrent, liquid-liquid extraction towers are used in which the solution is sprayed through the lubricating oil, removing the undesired materials. One common system uses furfural for this purification process. Another extracting material is a solution of phenol. The active material of the extract is recovered by distillation and decantation operations and sent back to the extraction operation.[49]

Liquid-Liquid Extraction Equipment—Liquid-liquid extractions are usually performed in continuous, countercurrent equipment. As is true in many cases in the chemical industry, the apparatus for bringing about efficient contact between two fluid phases is a simple tower. In the case of liquid-liquid extraction, it is quite frequently an open tower which is filled with one of the immiscible liquids while the other is sprayed up, or down, through it. Thus the tower might be filled with the liquid of lower specific gravity. The heavier liquid would be allowed to settle in droplets down through the other, and would be removed from the bottom by means of appropriate pumps or overflow devices. A continuous inflow of the lighter liquid would be maintained at the bottom of the tower, and it would overflow at the top. The procedure might be reversed and the tower filled with the liquid of greater specific gravity and the lighter liquid would be allowed to rise in drops through it. Sometimes the tower is filled with packing, which slows the passage of the drops and affords increased interfacial contact.

It is common practice to fill the tower with the so-called "continuous phase" of that liquid which is in greatest quantity and to send the other, either up or down the tower, in the form of drops or the "discontinuous phase." The material from which the soluble substance is being removed is the "raffinate" and the liquid phase which has picked up the soluble material is usually called the "extract."

Theory of Liquid-Liquid Extraction—As in all cases where there is a transfer of material from one fluid phase to another, the presence of the inert films at the interface are very important in the operation. Although liquid-

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[47] See Chapter 17.
[48] See Chapter 28.
[49] See Chapter 14.

liquid extraction has only recently been put on a quantitative basis the research work on the character of the films and their resistance to the transfer of material has been very fruitful. The prediction of performance for this operation tends to be rather complicated, because the solubility, or equilibrium, relations between the two phases are seldom simple. The situation is further complicated when the extract and raffinate are partially soluble in each other. Nevertheless, the study of this operation is now on a fairly satisfactory quantitative basis.

FILTRATION

The problem of removing finely divided solids from a solution by the operation of filtration has brought more or less grief to almost every student of elementary chemistry. If solid materials are relatively coarse, the problem of separation is one of simple settling followed perhaps by draining. Fine materials may sometimes be effectively separated from most of the water by means of "thickeners" described in a previous section.[50] The solid material in such cases, however, still contains considerable water in the interstices of the solids so that it is not sufficiently dried for many industrial operations. Whether or not a thickener is used, in order to remove the bulk of the water from a suspension of fine materials, it is almost always necessary to resort to filtration.

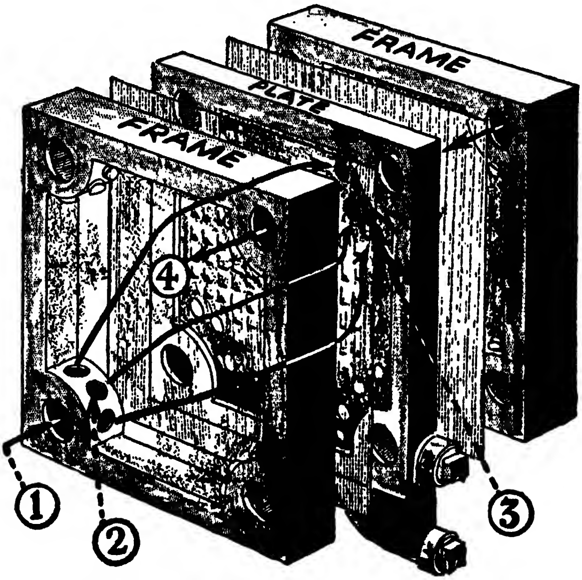

Fig. 29. Construction of Filter Plates.

Types of Filtration Apparatus—The types of industrial apparatus which are used for this operation logically fall into five different classes. (1) The sand filter which is described in a later chapter,[51] (2) Filter Presses, (3) Leaf Filters,

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[50] See p. 69.
[51] See Chapter 6.

(4) Continuous Rotary Filters, and (5) Centrifuges which, though truly not filters, may serve the same function.

Filter Presses—The filter press was one of the first devices used for filtration on a large scale. Although the different presses vary quite markedly in individual construction, they all operate on the same principle. The essential element of the filter press is a corrugated plate over which is stretched a filtering membrane, usually a close-knit cotton cloth, which serves the purpose of the filter paper in the ordinary chemical laboratory. These plates are arranged in series on a long frame and are alternated with open frames which afford space for the flow of the filtrate and for building up of the filter cake. The details of one type of plate construction are shown in Figure 29. These plates and frames rest on a pair of parallel bars and are held in position by lugs projecting from each side. A large number of them are arranged in series on the apparatus, the whole assembly being forced against the adjacent frame by means of a screw or hydraulic pressure. The assembly of a very large press is shown in Figure 30.

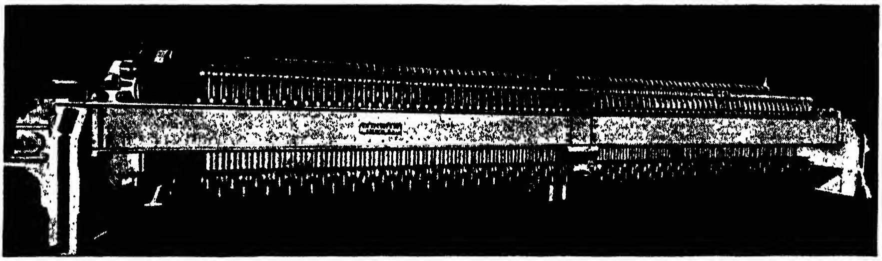

FIG. 30. Large Plate and Frame Filter Press. (Courtesy D. R. Sperry Co.)

The material to be filtered is forced through a channel, usually along the top of the press, and into the frame. The solid material is held back by the filtering medium and gradually fills the chamber, producing a solid cake. The liquid which passes through the filter is allowed to discharge into this channel along the lower part of the press where it may be recovered or discarded, as desired.

After the cake has more or less completely filled the frame, it may be washed, either by sending water through in the same direction as that which the sludge entered, or in the opposite direction.

Filter presses are obviously usable only for batch operations and the labor costs are quite high, hence, except for the more expensive materials, their use can be hardly justified, and they are being quite generally replaced by other types of filters.

Leaf Filters—The so-called Sweetland self-dumping leaf filter is shown in Figure 31. The filter body comprises two semi-cylindrical castings of high tensile strength, which are tightly bolted together during operation. The filtering medium is made up of the series of pancake leaves covered with filter cloth. The material to be filtered is forced into the filter body by gravity pressure or by means of a pump. As soon as the filter body is filled, the pressure rises, causing the liquid portion to pass through the filter cloth while the solid material is deposited on the leaf in a compact form. When the filter is full, the bottom half of the body is unbolted and lowered. Then by reversing the hydraulic pressure, the cake is readily pushed off the leaves and dropped into a container below.

Rotary Filter—This type of filter owes its wide use and success largely to the fact that it can be operated continuously and can handle large volumes of material at low cost. A type which is widely used is the Oliver Continuous Filter, an illustration of which is shown in Figure 32. Essentially, this filter consists of an open container in which is suspended a drum with the periphery composed of a number of shallow compartments covered with filter cloth or screen. Each compartment, by means of individual pipe line, is connected to a perforated trunnion which turns against a stationary valve cap attached to suction and blow lines. The arrangement is such that suction and air pressure may be applied at different points to each of the compartments during each revolution of the drum. In operation, the liquid is kept at a constant level in the container and thoroughly mixed by agitation. As the drum slowly rotates, suction is applied to the several compartments while they pass through the liquid to be filtered. The clear filtrate is drawn through the filtering cloth, leaving the solid deposited on the surface of the drum in the form of a cake. As the compartments emerge from the container (suction being continued), the cake is sub-

FIG. 31. Sweetland Self-dumping Filter.

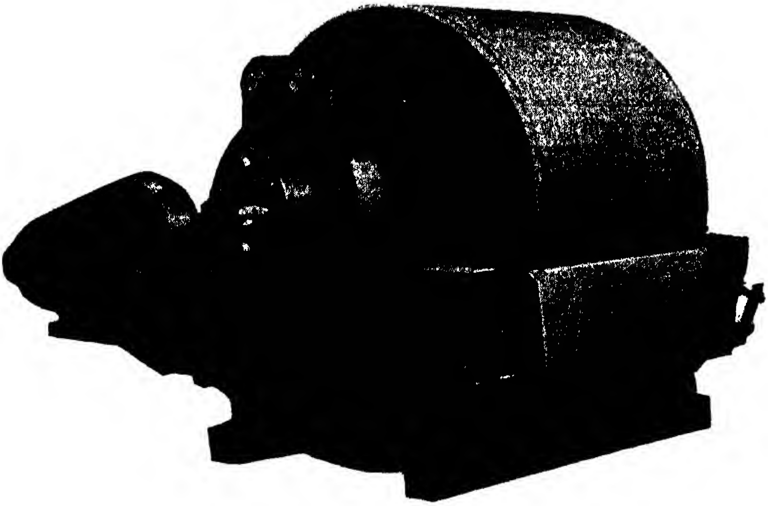

FIG. 32. Rotary Continuous Filter. (Courtesy Oliver United Filters, Inc.)

jected to a wash by means of a sprinkler equipment. Just before the compartments re-enter the container, suction is automatically cut off and air under pressure is applied causing the cake to discharge over an apron or "doctor" in the form of continuous ribbons.

This type of filter is extensively used for handling various kinds of chemicals, metallurgical products, beet sugar solutions, etc.

A modification of the continuous filter which bears some resemblance to the leaf filter is the so-called "American," shown in Figure 33. This is a disc type which operates by vacuum, each disc being made up of individual removable sections to facilitate filter cloth changes. It is used extensively for dewatering cement slurry, certain grades of coal, etc. A clever adaptation of the type of filter is found in the fairly recent string discharge mechanism illustrated in Figure 34. This mechanism makes it possible to convey the cake from the filter surface around a steam drum before discharging it, in order to perform a certain amount of drying in addition to the dewatering effect of the filtration. It is particularly applicable to relatively coarse materials or those which form fibrous cakes such as food products, paper pulp, sewage sludges, etc.

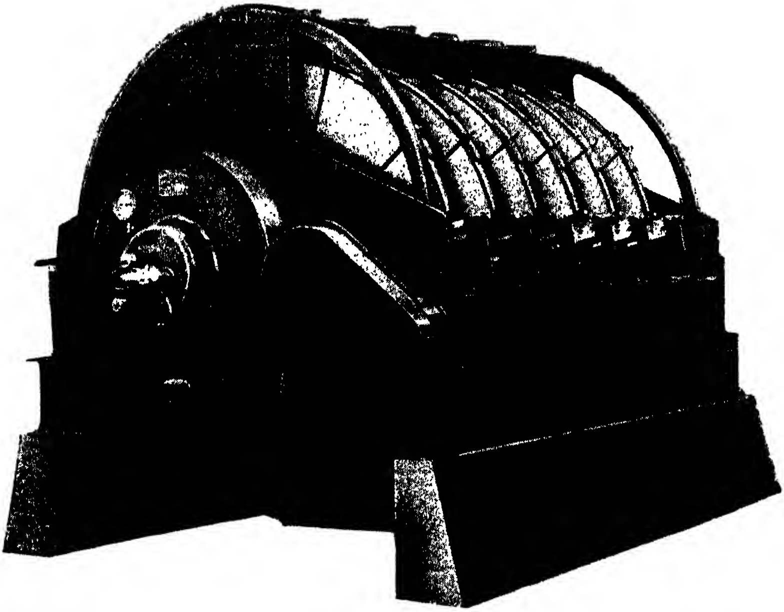

FIG. 33. American Continuous Filter. (Courtesy Oliver United Filters, Inc.)

Centrifuges—The centrifuge is especially adaptable for the separation of water from more or less coarse crystalline materials such as sugar, or ammonium sulfate, but since it offers the advantage of rapid operation and large production in small floor space, it is being improved and adapted to the use of finer and finer materials. An illustration of the bottom discharge centrifugal is shown in Figure 35. The principle of operation is that the mother liquor, with the crystals, is thrown out against the surface of the basket by centrifugal force. The cylindrical basket is perforated or lined with a fine wire gauze and rotates at a speed of 900 to 1200 revolutions per minute. Because of the large centrifugal force generated, the liquid is violently forced through the perforated basket and the crystals are left behind. This gives a definite drying effect in addition to the filtering operation. In addition to the use in the chemical field for sugar starch, wood pulp, etc., it is quite widely used for the dewatering of more bulky materials such as yarns, textiles, etc., and finds very wide use in the laundering field.

Filtration Theory—Filtration is certainly one of the older unit operations, but its quantitative theoretical consideration has been very sadly neglected until quite recently. The apparatus and methods largely evolved by rule of thumb methods, and as long as these worked satisfactorily there seemed to be but little call for fundamental theoretical developments. However, in recent years there has been considerable development along this line so that it is now possible to make fairly accurate predictions for the design and operation of a given type of filtering equipment, provided a very small amount of data is available from simple filtration experiments upon a laboratory sample.

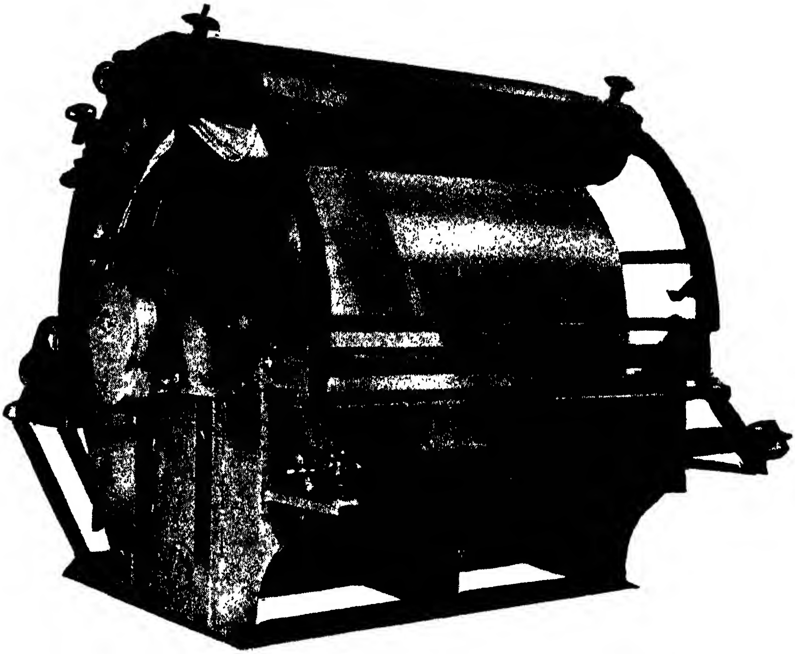

FIG. 34. Continuous Rotary Filter with String Discharge Mechanism. (Courtesy Filtration Engineers, Inc.)

In its simplest fundamentals, the filtration problem is merely that of fluid flow, that is, the flow of the liquid through a cake of the material which has been separated. A complicating feature is brought about by the fact that as the filtering cake builds up, it not only increases in thickness but also, quite frequently, in compactness. This means an ever-increasing resistance to fluid flow Despite the complexities of the case, fairly satisfactory semi-empirical relations have been worked out, and further advances may very well be expected along this line.

Filter-Aids—A common and irritating phenomenon in the chemical laboratory is that of a colloidal suspension of solid material which passes through any filter paper or filter cloth. If the solid material which is to be removed is of no value, such as is usually the case in the purification of sugar, chemicals, oils, fruit juices, varnish, etc., then these colloidal particles can usually be filtered out by means of the use of filter-cel or other types of filter aids. Filter-cel is a diatomaceous earth or kieselguhr, relatively finely divided siliceous material which has high absorptive capacity for colloidal properties. This granular material is itself incompressible and if it is mixed with the solution to be filtered it very effectively adsorbs the colloidal materials and permits both the filter aid and the finely divided solids to be separated from the liquid. In many cases precipitated calcium carbonate. or other granular crystals may be used as filter aids.

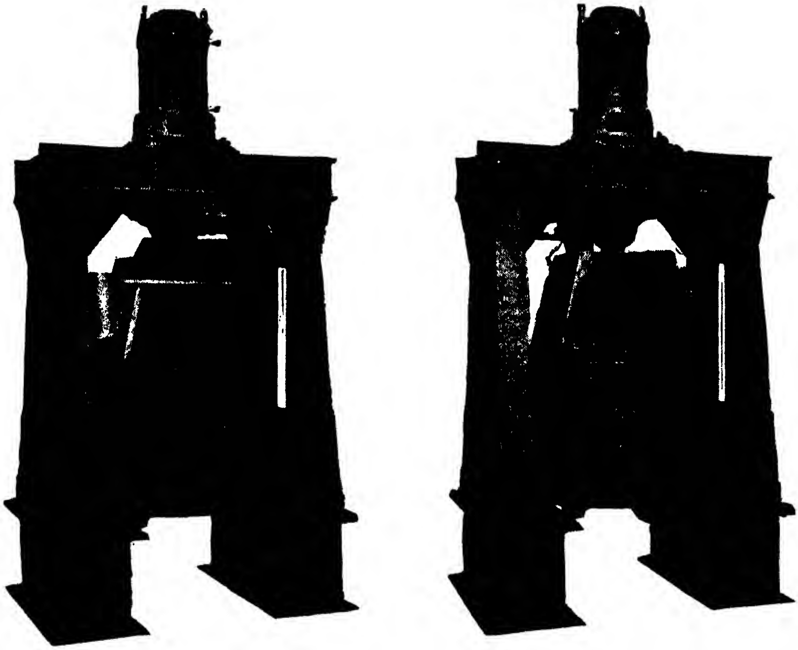

Fig. 35. Bottom Discharge Suspended Centrifugal. (Courtesy American Laundry Machinery Co.)

CRUSHING AND GRINDING

Wherever solid materials are used in chemical industry, there is almost always some application of the operation of crushing and grinding to reduce the size of the material so it may be more readily used for chemical reaction or for mechanical handling or for separation operations.

This operation arose from the background of one of the older mechanical arts and has practically no integrated theoretical background. The evolution of the equipment came from many isolated points of development and, just as there is very little in common in the evolution of language between isolated groups, there is relatively little unity between different types of crushing and grinding equipment. However, there is a certain common basis of operation which affords a fairly satisfactory means of classification and discussion.

In general, crushing refers to the breaking-up of solids into coarse materials. It might apply to the disintegration of natural ores from very large pieces down to particles of the order of one-quarter to two inches in diameter. Grinding in general refers to the finer pulverization of materials, say to sizes less than one-quarter of an inch, on down to fine dust a few microns in diameter.

Although the types of physical operations involved are not entirely clean-cut, it may be said that there are three methods by which crushing and grinding is carried out. First is the matter of the mechanical squeezing, so that the material fails in compressive stresses. A second pulverization mechanism is that of impact, where kinetic energy is used to bring about disintegration of the particles. A third rough classification is that of applying sheer stresses, giving the general effect of literally pulling apart the different particles of a solid body.

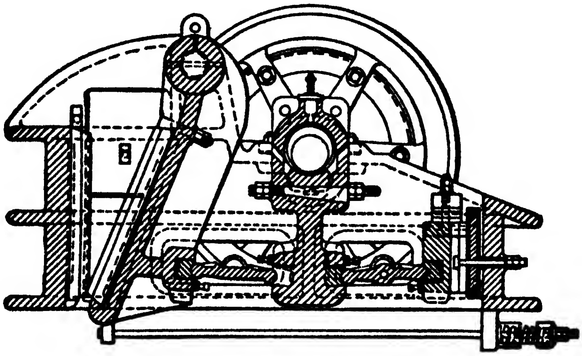

FIG. 36. Cross Section of Jaw Crusher.

Coarse Crushing—A rapid glance at a catalogue of crushing equipment would leave one with the impression that there is almost no unanimity of opinion among different equipment manufacturers as to what the best devices are. However, there are some half a dozen standard forms which are now most widely used.

The *jaw crusher* is the simplest and least expensive device. It is a very heavy machine and consists essentially of a stationary steel plate against which a corresponding steel jaw works on a cam, imparting a reciprocating or a combination or a reciprocating and sliding motion. This machine will crush the hardest materials, provided the steel plates have sufficient hardness and strength to withstand the work. The working parts may be regulated by means of an adjusting screw, to give a fine or coarse product. It is applied to very large extent in metallurgical operations for ore crushing and for such more purely chemical operations as the crushing of pyrites for sulfuric acid manufacture. A cross-section diagram of a jaw crusher is shown in Figure 36.

Crushing Rolls. Two hard steel rolls running in opposite directions and set close together make a very effective device for crushing to intermediate size. The rolls may be either plain or corrugated, either one or both of which may be positively driven. The latter is usually the case. They consist of two heavy cylinders on a horizontal plane and the clearance may be so adjusted as to reduce to any intermediate size. The best results are obtained when the rolls travel at moderate speed. A cross section of a roller crusher is shown in Figure 37.

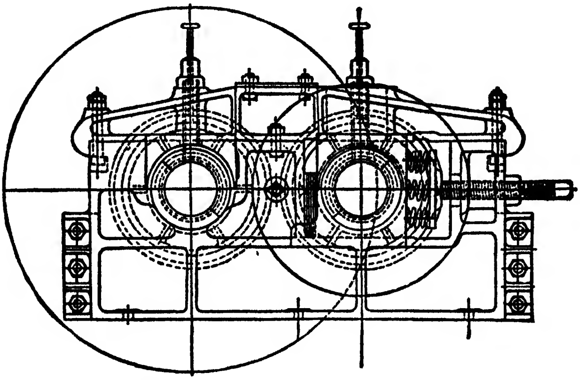

FIG. 37. Cross Section of Roll Crusher.

The *gyratory crusher* consists essentially of a conical vertical shaft which operates on an eccentric bearing at the bottom. This motion squeezes the material between the shaft and the side wall. The shaft is fixed at the top, and the eccentric bearing at the bottom causes the lower part of the shaft to wobble, not to rotate. This gyration promotes crushing by the alternate advance and recession of the shaft. This crusher reduces rock in successive stages, in that the larger pieces are first broken and each succeeding nip reduces the fragment to a still smaller size.

Hammer Mills. The swing hammer crusher is used on soft rock, lime, and other material which is easily broken. It consists essentially of a central shaft to which are attached a number of heavy hammers so pivoted as to swing freely. As the shaft revolves at a high speed the hammers swing out by centrifugal force and come in contact with the rock which is being fed over the breaker plates. On the under part of the machine is a grid of steel bars through which the crushed rock can pass only when it has been sufficiently reduced by the revolving hammers. The size of the delivered material is regulated by the spaces between the grid. See Figure 38.

FIG. 38. Swing Hammer Crusher. (Courtesy Greundler Crusher and Pulverizer Co.)

The *rotary crusher* consists of a corrugated metal cone revolving with small clearance between it and corrugated side plates. It will handle rocks of moderate hardness. The crusher is provided with double doors, carrying the grinding plates, which can swing open easily, thus exposing every part for inspection and cleaning. The capacity of the machine and the size of the broken material can be adjusted by a screw which regulates the clearance between the revolving cone and the plates. This type of crusher is illustrated in Figure 39.

Fine Grinding—The *disintegrator* is a very simple machine consisting of steel cages which run at a high speed in opposite directions, thus driving the material through the steel bars by centrifugal force and pounding it into a powder. An illustration of this type of machine is given in Figure 40, which shows the casing of the mill removed and the revolving cages pulled apart for inspection. This machine must be strongly built but it can easily be taken apart and easily and quickly cleaned by taking off the top half of the casing. It is mostly used for materials of a lumpy nature, like dry colors, soft pigments, borax, sulfur, starch, etc., and it also serves as an effective means of simultaneously mixing and grinding dry materials, like fertilizer.

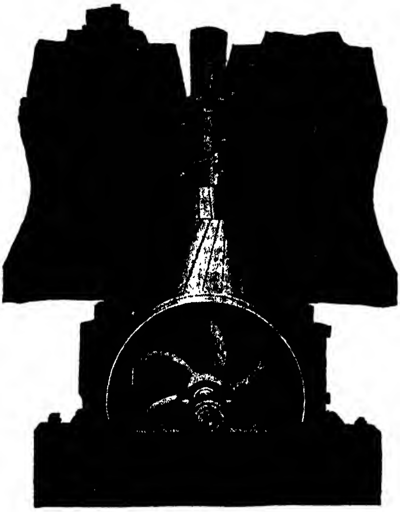

FIG. 39. Rotary Crusher.

The *buhr-stone mill* is probably the oldest type of grinding machine which is still in use. It survives in some places despite the many changes and improvements that have been made in other types of equipment. It consists, essentially, of two horizontal stone pancakes which are corrugated, with one stone revolving while the other is fixed. At one time it was universally used for the grinding of flour, and is still used in the disintegration of products for making corn products.[52] In addition, it is used in the making of paints, printer's ink, cosmetics, and pharmaceutical preparations. An underdriven mill is shown in Figure 41. The material is fed in through a hopper and is carried by centrifugal force to the grinding parts of the first set of stones, from which it then passes to a second step for finer grinding. Buhr-stone mills may be operated either wet or dry.

The *disc mill* might be considered to be a modification of the buhr-stone mill. It consists of two iron discs set close together, one of which rotates. They may be plain or corrugated. Usually the shaft carrying the discs is set in a horizontal plane. The shaft of the moving disc is set with a slight eccentricity, so the grinding discs approach one another at one part of the periphery and separate at another part. This gives a combination of squeezing and shearing action. By adjusting the clearance this device may be used for either fairly coarse crushing or relatively fine grinding.

The *pan mill,* or as it is sometimes called, the edge runner or chaser, is used for breaking relatively soft materials up into fine powders. It is widely used in the clay industry for preparation of clay for working.[53] It is also used for the

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[52] See Chapter 36.
[53] See Chapter 21.

preparation of printing inks and pharmaceuticals. This mill consists of a steel bed built with sloping sides to form a pan on which rotate one or two "edge runners" or "travelers." An arm, with a scraper attached, travels just in front of the runners and brings the material under the heavy rolls. As they travel around the pan this gives a combined crushing and shearing action which is very effective in producing fine states of subdivision. It is also an effective mixing device, where it is desired to make a fine paste.

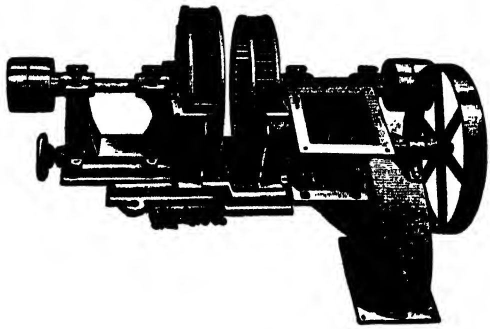

FIG. 40. Disintegrator, or Pulverizing Mill, with Cover Removed.

Ball mills grind principally by the impact and shear produced by the sliding, tumbling, and rolling of a large number of steel or flint balls or pebbles which are mixed with the substance to be ground, the movement being caused by revolving the mill at a regulated speed. This type of apparatus which is very common in chemical laboratories is shown in an enlarged scale in Figure 42. This is a batch device and must be stopped and discharged after the grinding has been carried to the desired point.

The *tube mill* is essentially the same as the ball mill except that it is arranged so that it can operate continuously. The material to be ground is fed in at one end and it is delivered as a finished product at the other. The fineness of the materials is regulated by the speed at which the material is fed. The slower the feeding, the longer the material receives the impacts of the pebbles and the finer the discharged product. An adaptation of this mill is the so-called Hardinge conical mill which is shown in Figure 43. This mill contains pebbles or balls of several different sizes. The large crushing bodies arrange themselves in the largest diameter and decrease in size toward the outlet of the cone. The coarse material entering the mill is immediately subjected to the impacts of the largest grinding bodies, is subdivided, and, according to the division, is passed along to the next zone of smaller grinders and so on until the discharge end is reached. This makes ideal equipment for taking large material and grinding it to very small size.

FIG. 41. Buhr-stone Mill.

The *rod mill* is essentially the same type of apparatus as the tube mill except that long steel rods lying horizontally are used for the crushing mechanism.

The *colloid mill* may be considered an ultra-fine grinding device, but it may serve one of two different functions: first, the grinding of solid materials to very fine state of subdivision and to a high degree of dispersion; second, the homogenization of a liquid. In a "homogenizer," immiscible liquids pass simultaneously at high pressures through specially designed valves and produce a very fine emulsion due to the shearing action.

The apparatus which is commonly known as a colloid mill operates with two controlling factors, speed of rotation and grinding area. One type of mill has two smooth rotors revolving in opposite directions, thus giving a maximum of shearing stress. In the colloid mill it is essential that the gap between the rotating plates, or a rotating plate and its containing surface wall, shall be very small and the speed of rotation shall be very high. Some mills rotate as high as 20,000 revolutions per minute. Because of the small clearances involved, such a mill will handle only pastes where the solid material is already quite finely divided. One type of colloid mill is shown in Figure 44.

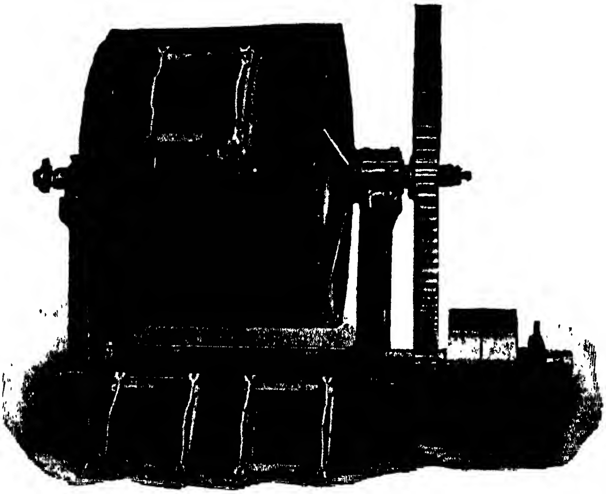

Fig. 42. Ball Mill.

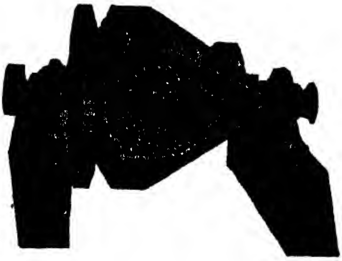

Fig. 43. Hardinge Conical Mill.*

Among the many operations for which the colloid mill is well adapted are the emulsification of vegetable, animal, and mineral oils, resins, waxes, etc., incorporation of pigments in the more fluid enamels, preparation of calcimines, extractions of oil, fats, juices, etc., from vegetable or animal tissues, extraction of fibrous material, intimate mixing of various food products, increasing the solubility and surface area of insoluble products through fine dispersion, blendings of creams, sauces, and other food products, dispersions of solids and liquids such as the preparation of vat dye paste and a number of other products

SEPARATION OF SOLID MATERIALS

One of the most common operations in chemical as well as metallurgical industries is the separation of solid particles from one another. This separation may be for differences in size or it may be for differences in kind of materials, or both. For instance, if the hard part of a natural ore is a valuable and desired constituent, and the other one is soft, crushing will grind up the undesirable material finer than the other and hence a simple screening operation after grinding will largely separate the two materials.

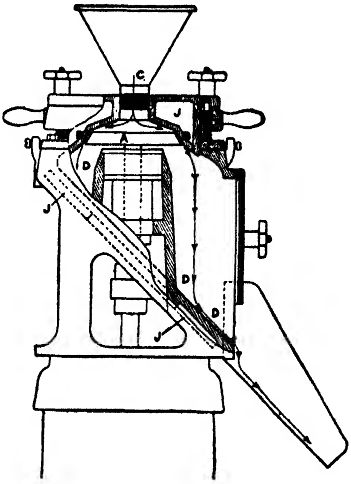

Fig. 44. Cross Section of Paste Type Colloid Mill. (Courtesy Premier Mill Corp.)

Screens—The commonest method of size separation is that of screening, which consists simply of passing material through an open mesh wire screen by the means of some sort of agitation. The larger material stays on the screen and the finer goes through.

The types of screens are as follows: Grizzlies, which are a set of rods or screens set on an angle with the material to be separated rolling down over it. Trommels are rotating screens used for fairly large particles. Shaking screens are used for minor sizing. Vibrating screens which have a vertical, rapid vibration of small amplitude are used for quite fine sizing. The smallest common commercial screens will separate particles down to about 200 mesh. If the separation of finer particles is necessary, then other devices must be used, and for most fine particle separations it is usually much more economical to use methods other than screening.

Air Separations—Separation of solid particles from an air stream is sometimes known as air filtration but this is more or less of a misnomer.

The commonest type of air separation device is the cyclone separator which depends upon the well-known principle that solid particles, due to their inertia, will drop out of an air stream if the direction of flow is suddenly changed. There is also a similar effect of the centrifugal force: throwing particles out to the outside wall of the container. Another common device is the bag filter where the air is forced through a fine-mesh cloth in the form of a cylindrical bag. The various mechanical air separators on the market are usually modifications of these two devices. The diagram of an air separation circuit in connection with the grinding mill is shown in Figure 45.

Electrical Precipitation—The Cottrell apparatus is one of the most widely used devices for removing very fine particles from an air stream. The operation consists of passing gases through conduits of relatively small cross sections each having a central electrode which carries a uni-directional, high voltage, usually about 50,000 to 60,000 volts.

Solid particles passing through the tubes become electrified and attach themselves to the electrodes. A mechanical tapping arrangement jars the electrode and the accumulated dust falls into a hopper below. If it is used to collect liquid mist, the liquid layer will drain down the tube. The Cottrell apparatus has been successfully used for the removal of fine dust from all kinds of waste gases, for example, the precipitation of fine copper or arsenic oxides from smelter gases and the precipitation of potash bearing dust from cement kilns are common applications. These precipitators are also used for the removal of acid mists in many processes. They find extensive application of removal of particles of tar and water from manufactured gas.

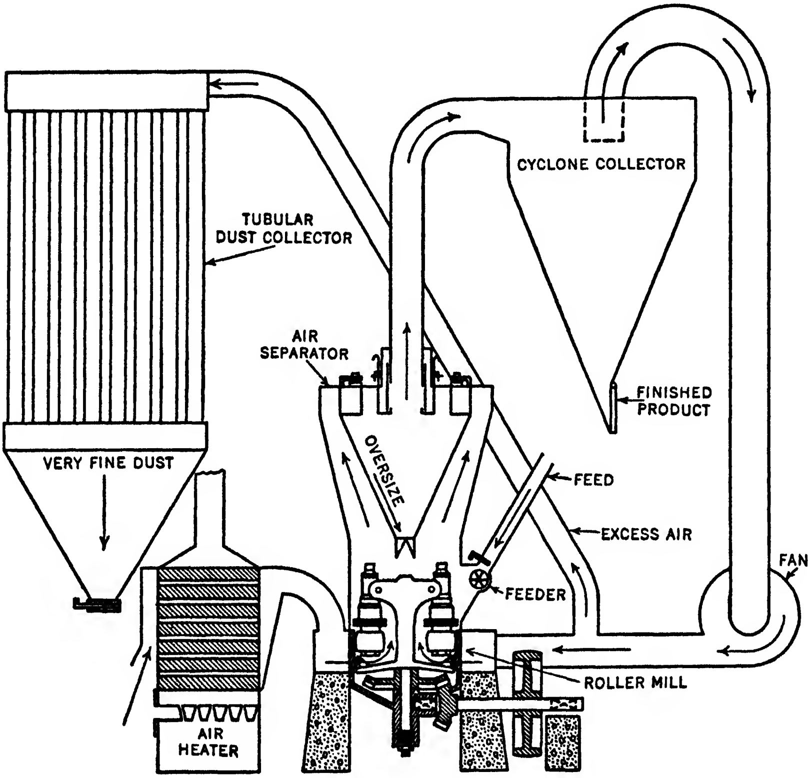

Fig. 45. Grinding Mill with Air Separation System. (Courtesy Williams Patent Crusher and Pulverizer Co.)

Hindered Settling in Liquids—In the separation of solid materials extensive use is made of the fact that large particles settle through a liquid faster than small ones, also, the greater the specific gravity, the faster the rate of settling. A good example of this is seen in a small settling pond where a muddy stream comes in at one end and the larger particles settle to the bottom and the water leaves partially clarified at the other. The simplest type of hindered settling consists of running a sludge of solid materials into a large container and then allowing the liquid to overflow at an appropriate rate. The water stream carries out the fine particles and leaves the large ones behind. By combining the effect of the lifting component of a fluid stream plus mechanical rakes, it is possible to devise "classifiers" which can be very efficient in separating sizes. The more common type Dorr classifier is shown in Figure 46. The Dorr classifier is a reciprocating rake machine for separating coarse or heavy particles from fine ones. The critical size at which separation is made can range from 10 to 325 mesh, depending on the tank slope, rake speed, and feed dilutions.

All these devices for hindered settling also serve to effect separations between particles that have different specific gravity.

In the metallurgical field, one of the most common devices for hydraulic classification is the jig, in which an alternating motion is given to the suspending water, which gives a particularly good separation between fine or light materials and heavier ones which settle to the bottom of the apparatus. For small particles, the Wilfley table combines cross washing with a longitudinal jerking motion in a thin liquid layer flowing over a corrugated table.

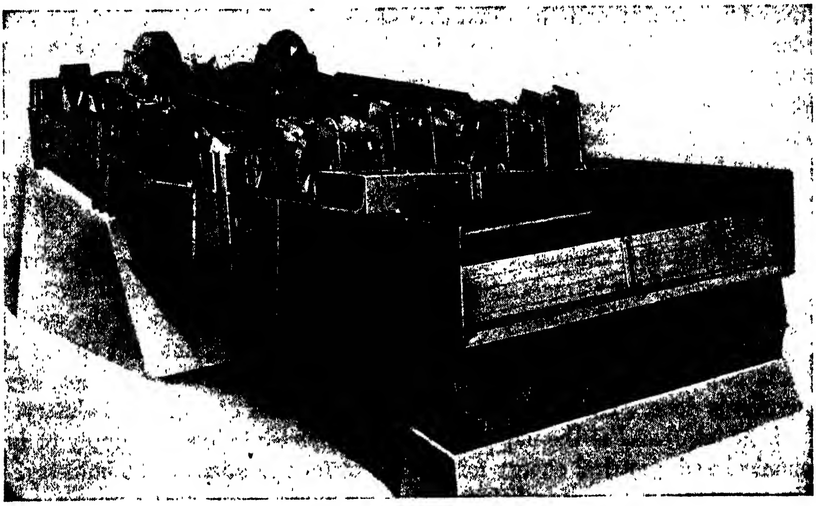

FIG. 46. Dorr Classifier. (Courtesy Dorr Co.)

Flotation—Many materials, particularly metallic ores, can be separated by the method of flotation, which is based upon the selective wetting of different solid particles by various organic substances. For instance, sulfide ores are not wetted with water, if certain of the flotation agents such as xanthates are present, while silicate and oxide particles are wetted. If the liquid is agitated with air, a froth is formed and the unwetted particles rise with the foam, while the wetted particles sink. Thus the sulfide ore particles contained in the froth can be scraped off by a suitable mechanical device. This operation of flotation has very wide use in the non-ferrous metallurgical field.[54] It is coming more and more into use in the separation of different kinds of non-metallic minerals, particularly in the cement industry.[55] Experimentation along this line involves a special branch of physical chemistry and undoubtedly there will be much more development in

[54] See Chapter 24.

[55] Englehart, G. K., Ind. and Eng. Chem., *32*, 645 (1940).

the future for this type of mechanical separation, as research work leads to a more complete understanding of the phenomena.

MISCELLANEOUS CONSIDERATIONS OF THE UNIT OPERATIONS

The foregoing very sketchy descriptions in this chapter are intended to furnish the reader with the most essential points of the background of the physical operations which are an integral part of the processes of chemical industry. The list of the subjects considered is not necessarily complete, for there are other physical operations which might logically fall in the field of the unit operations. As is the case in the study of any extensive field, the subdivisions might be greatly increased in number and the discussion of details could go on endlessly, so the reader certainly should not consider that this presentation has been an exhaustive survey of the subject. He will also notice that there have been no quantitative engineering considerations in the treatment. For actual application of the knowledge involved, it is necessary to go in for a program of very serious study in the particular field of interest. But the authors feel that the treatment has been sufficiently exhaustive to give one a general understanding of the most important aspects of the subject.

Energy for the Chemical Industry—It may have been noted throughout the discussions of the various operations that almost all of them call for the use and control of a considerable amount of energy. The description of the workings of the various individual chemical industries will also bring out that energy is of extreme importance, as a matter of fact, an absolute essential in almost everything that is done. The more one investigates the field of chemical industry, the more is he impressed of the importance of a completely adequate supply of fuels, mechanical and electrical energy for the successful operation of the industry. In order to maintain a proper balance of the consideration of the importance of the field, it is necessary that one keep in mind this item of the paramount importance of the energy supply.

Undoubtedly it would be desirable to have a lengthy chapter devoted to the consideration of the uses of fuels and the generation and control of energy in the chemical industry, but limitations of space would make it necessary to confine such a discussion to an extremely sketchy treatment and such casual handling of the matter would serve no useful purpose. Hence, the energy considerations have been left to the incidental treatment in the chapters which discuss the individual industries.

Materials of Construction—Proper materials of construction of the equipment for the chemical industry fall in the same category of importance as fuel; that is, absolutely essential. The chemical engineer is faced with a doubly difficult problem when it comes to selection of materials. In general, it may be said that a mechanical engineer, for instance, is concerned almost entirely with the materials which will live up to certain expectations of strength, which in itself leads to a number of complications and difficulties. The chemical engineer, on the other hand, must not only consider strength but he is continually confronted with the bugbear of corrosion. The very nature of the materials which he handles makes it unavoidable that corrosion is one of the items which will always be with him. The balancing of items of strength requirements, corrosion resistance, and economic consideration is one of the most important functions of a chemical engineer. The items involved are so many and the field is so complicated that here, again, a very brief treatment such as might be allowed in the space available in this volume, would be of but little utility; hence, it seems best to leave the subject here with bare mention of its importance. Frequent mention and some discussion of the materials of construction will be found in the chapters dealing with the individual industries.

READING LIST

GENERAL

There are a few sources of information on the quantitative aspects of the various Unit Operations which are very comprehensive and fairly complete, on both principles and descriptions of equipment.

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Perry, J. H., "Chemical Engineer's Handbook," second edition, McGraw-Hill Book Co., New York (1941).

Walker, W. H., Lewis, W. K., McAdams, W. H. and Gilliland, E. R., "Principles of Chemical Engineering," third edition, McGraw-Hill Book Co., New York (1937).

These references will not be repeated under the individual unit operations but it is well to consult them in all cases.

For illustration and descriptions of equipment a great deal of information can be gained from the descriptive catalogs of equipment manufacturers. A convenient, comprehensive, and profusely illustrated compilation of chemical engineering equipment will be found in

"Chemical Engineering Catalog," Reinhold Publishing Corp., New York. Published annually.

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CHAPTER 3

THE ORGANIC UNIT PROCESSES

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INTRODUCTION [1]

Organic chemistry or the chemistry of carbon compounds deals with more than 250,000 compounds. While at the present time many of these compounds are merely scientific or laboratory curiosities, a very large number of them find various applications in our industries and in our daily life. The production of dyes, dye intermediates, fuels, solvents, explosives, disinfectants, insecticides, antiseptics, drugs, perfume materials, flavoring substances, food preservatives, synthetic resins, plastics, rubber accelerators, flotation agents, synthetic tannins, synthetic rubber, synthetic fabrics, lacquers, photographic chemicals, soaps, pharmaceuticals, poison gases, sweetening agents and various other topics mentioned in this volume belong to the realm of industrial organic chemistry.

For a number of years the term "industrial organic chemistry" referred to a large amount of information of a descriptive or qualitative nature concerning the industrial preparation of various organic compounds and compositions. Though this information was valuable, it could not be used as a basis for the scientific design of process equipment or for the industrial preparation of these chemicals as the quantitative aspects were lacking. Hence, the design of equipment and the selection of operating conditions were largely effected by rule-of-thumb methods. A few years ago, however, this situation was remedied somewhat by the introduction of the idea of "unit processes" [2] as a basis for correlating the available information concerning industrial organic chemistry into a more useful form. With the unit processes as a framework, hundreds of isolated facts and principles were classified under a few main headings. This classification has been of great value to manufacturers, to research workers, and to designers as it has emphasized the wide applicability and utility of the fundamental principles underlying each of the unit processes. It has stimulated much valuable research which has resulted in technological advances in all phases of the industry. In spite of the advances that have been made, much remains to be done before the unit

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[1] Some of the material in this introduction was borrowed, with the author's permission, from Dr. Alexander Lowy's chapter on Industrial Organic Chemicals and Dye Intermediates published in the Fifth Edition of this Manual.

[2] "The term 'unit processes' is used here to represent the embodiment of all the factors in the technical application of an individual reaction in organic synthesis." [Quoted from the preface to the first edition of "Unit Processes in Organic Synthesis" by P. H. Groggins. McGraw-Hill Book Co., Inc., New York.]

processes can be put on a completely quantitative basis. Their present status might be likened to that of the unit operations twenty-five years ago, the remarkable development of which has already been described.[3] It seems reasonable to hope from the analogy to the unit operations that many of the unit processes will be put on a quantitative basis before many more years have elapsed.

In this chapter the fundamental principles and factors involved in the most important unit processes are discussed. Because of the limitations of space, the discussions are brief and in general terms. Information concerning applications of these principles to specific materials may be found in other chapters in this book and in the references listed in the bibliography at the end of this chapter.

Basis of Classification—The unit processes are based on types of chemical reactions, such as sulfonation, halogenation, oxidation, etc. With respect to the chemistry involved organic chemists have made and are making many valuable contributions to our knowledge of such reactions. From an industrial standpoint, however, the chemistry of a process is only the beginning. It must be tied up with the physical aspects, the equipment needed and the economics involved. Hence, to design and operate equipment for carrying out processes on a commercial scale much more information is necessary than is usually obtained under the almost ideal laboratory conditions where the material is first prepared. The following information is needed over a wide enough range of conditions to permit the optimum conditions to be determined: (1) the yield that can be expected; (2) the time necessary to carry out the reaction; (3) the kind of apparatus suitable, and (4) the cost per unit of product.

The first item is concerned with equilibrium conditions; the second relates to reaction rates (chemical kinetics); the third is dependent upon the materials used and the type of process; and the fourth is concerned with economics. In the following pages a few generalizations regarding reaction rates and equilibria are presented. The fundamental factors and principles involved in each of the unit processes are then discussed along with a brief discussion of the type of apparatus used. The economic aspects are considered to be outside the scope of this chapter.

EQUILIBRIUM

A system is said to be in equilibrium when all forces and reactions are balanced by other forces and reactions so that no net change takes place with time. All spontaneous processes tend to approach a state of equilibrium and remain in equilibrium so long as external conditions are unchanged. Equilibrium conditions therefore represent the maximum yield that can be expected from a given reaction. In industrial processes it is necessary to know the effect of the important variables on the equilibrium so that the optimum conditions can be determined. In general, LeChatelier's principle can be used to make qualitative forecasts of the effect of changing one of the operating variables. According to this principle, if a stress is applied to a system in equilibrium, the equilibrium will tend to shift in such a way as to relieve the applied stress. The conclusions reached from the application of this principle are, in general, similar to

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[3] See Chapter 2.

those discussed below[4] for which quantitative calculations can be made. This principle has been a very useful generalization to guide research work even though the quantitative aspects are lacking for many cases.

Quantitative information on the effect of changing one of the important variables on a system in equilibrium is highly desirable wherever it is possible to obtain it. For many systems it is possible to make such calculations with a reasonable degree of accuracy by means of the equilibrium constant for the reaction. The equilibrium constant is a number characteristic of a given reaction at a given temperature and is independent of pressure or concentration. The familiar mass-action law expresses the relation between the "active-masses" of materials present in a system and the equilibrium constant for the reaction taking place. For reactions taking place under conditions such that the reactants may be considered as ideal gases, partial pressures may be used as active masses, while in dilute solutions of non-ionized substances concentrations can be used. For other homogeneous systems the activity function can be used.[5] Hence, the equilibrium constant makes it possible to calculate the quantitative yields that can be expected from a given reaction if sufficient data are available to evaluate the constant. Equilibrium constants may be evaluated from direct experimental methods or by calculation by thermodynamics using the free energy concept.[5, 6, 7, 8, 9] The experimental method is laborious and in many cases may not be reliable unless extreme precautions are taken. The thermodynamic method is also limited by the lack of accurate thermal data but even where accurate data are lacking, approximate data are useful for indicating trends and tendencies.

Once the equilibrium constants at various temperatures are known, it is possible to calculate the effect of the principal variables on the equilibrium conversion[10] under various conditions provided the necessary data are available. Methods of carrying out such calculations have been clearly explained in the literature[5, 6, 7, 8] and need no further discussion here. From such calculations and the Principle of LeChatelier certain generalizations are evident and are worthy of consideration. These are as follows:

1. The equilibrium conversion[10] of an endothermic reaction is increased by a rise in temperature, while the equilibrium conversion is decreased by a rise in temperature in the case of an exothermic reaction.
2. Pressure affects the equilibrium conversion of a gaseous reaction in which there is a change in volume due to a change in the total number of moles of gaseous components. If a reaction produces a decrease in volume, the equilibrium conversion will be increased by an increase in pressure. If

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[4] See p. 105.

[5] Hougen, O. A., and Watson, K. M., "Industrial Chemical Calculations," Second Edition, John Wiley & Sons, Inc., New York, 1936. Especially pp. 438-466.

[6] Ewell, R. H., Ind. and Eng. Chem., *32*, 147-53 (1940).

[7] Dodge, B. F., Trans. A. I. Ch. E., *34*, 529-67 (1938).

[8] Lewis, G. N., and Randall, M., "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York (1923).

[9] MacDougall, F. H., "Thermodynamics and Chemistry," Third Edition, John Wiley & Sons, Inc., New York (1939).

[10] The term "equilibrium conversion" as used here refers to the fraction of the limiting reactant present initially which is converted to products when equilibrium has been established under the given conditions.

there is no change in volume, pressure is without appreciable effect. If a reaction produces an increase in the number of moles of gaseous components, the equilibrium conversion will be decreased by an increase in the total pressure on the system.

3. The presence of an excess of one reactant tends to increase the equilibrium conversion of the other reactants present.
4. The addition of one of the reaction products to the initial reacting system will decrease the equilibrium conversion of the reaction. Likewise, removal of one of the reaction products as soon as formed will increase the equilibrium conversion of the reaction.
5. Dilution of a reacting system with an inert gas has the same qualitative effect as decreasing the total pressure on the system. If the reaction produces an increase in the total number of moles of gaseous components, dilution with an inert gas will increase the equilibrium conversion. If there is no change in the total number of moles of gaseous components, dilution with an inert gas will have no effect on the equilibrium conversion.

In making and interpreting calculations of the equilibrium conversion for a given system, the limitations of such calculations should always be borne in mind. Equilibrium calculations are made for a single reaction, though it is possible to calculate the equilibrium conversion for certain cases where more than one reaction takes place. Many organic reactions involve a complex mechanism and are complicated by side reactions to an extent which cannot be predicted by theoretical considerations alone. Equilibrium calculations for such systems are of no value in predicting what will happen when the reaction is carried out experimentally. However, if the reaction can be carried out in a manner to give primarily one product, equilibrium calculations can be of great value. Reactions of carbon monoxide and hydrogen furnish examples of both types of reactions. By the proper selection of catalysts and operating conditions, it is possible to carry out the reaction between CO and H_2 to give primarily methanol. Under these conditions calculated equilibrium conversions agree quite well with those obtained in commercial practice, and such calculations have been of great value in the development of synthetic methanol. On the other hand, in the Fisher-Tropsch synthesis, the same materials are reacted in the presence of a different type of catalyst under operating conditions but slightly different from those employed in the methanol synthesis, and a whole series of complex liquid products are obtained.[11] Obviously in cases of this sort where it is impossible to predict what products will be obtained, equilibrium calculations are of no value.

It should be emphasized also that the equilibrium conversion is the limiting condition toward which the reaction is directed and beyond which it cannot go. Industrial reactions, however, usually are not allowed to reach equilibrium but are stopped at some intermediate point because of economic considerations. Hence, the actual extent to which a reaction will proceed depends upon the rate of reaction, and the time allowed for it to proceed, as well as on the limiting equilibrium composition.

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[11] Underwood, A. J. V., Ind. and Eng. Chem., **32, 449-54** (1940).

REACTION RATE

The rate at which a reaction proceeds is determined by a number of factors: the order and mechanism of the reaction, the active masses present, the character of the system, the temperature, the presence of catalysts, the pressure, the energy of activation, side reactions, successive reactions, reverse reactions, etc., all affect the rate to a certain extent. Although no general procedure has been developed for weighing the effect of each of these factors on a given reaction for the purpose of exactly predicting the reaction rate, certain principles have been developed which are useful in a qualitative or semi-quantitative way.

Order of Reactions—The relation existing between the concentration of the reactants and the rate of reaction determines the order of a reaction. If the rate of reaction is directly proportional to the first power of the concentration of a single reactant, the reaction is said to be a first order one. Second order reactions are those in which the rate of reaction is proportional to the product of the concentration of two reacting molecules, while third order reactions are those in which the rate of reaction is proportional to the product of the concentrations of three reacting molecules. The probability of reactions of an order higher than third order is so remote that they are given no further consideration. It should be pointed out at this point that it is not possible to predict the order of reaction by merely writing down the equation for the reaction. The order of reaction does not necessarily bear any relation to the ordinary equation used to represent the reaction, but it must be determined experimentally. Reaction rates do not necessarily fit in with any "order" as defined above. On the other hand, certain reactions do approximate first order reactions even when heterogeneous.

First order reactions ordinarily involve a single reactant molecule *A*, which decomposes into products as follows:

$$A \rightarrow B + C + D \ldots\ldots$$

If n_A = moles of *A* per unit mass of reacting system, t = time, and k is a constant (reaction velocity constant) a first order reaction can be expressed by the equation

$$\frac{-dn_A}{dt} = kn_A$$

which on integration gives

$$ln \frac{n_{A0}}{n_A} = kt$$

where n_{A0} = moles of *A* present in a unit mass of system when $t = 0$.

Analogous equations for second and third order reactions may be formulated.[12, 13, 14] In the cases of homogeneous gaseous reactions carried out under conditions such that the ideal gas laws apply, such equations show that the rates

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[12] MacDougall, F. H., "Physical Chemistry." The Macmillan Company, New York, 1937, pp. 399-443.

[13] Getman, F. H., and Daniels, F. "Outlines of Theoretical Chemistry." McGraw-Hill Book Company, Inc., New York.

[14] Article by K. M. Watson on "Chemical Kinetics" in Monograph published by A. I. Ch. E. on "Teaching of Chemical Engineering." New York. 1940.

of second order reactions are directly proportional to pressure while third order reactions are proportional to the square of the pressure. Under the same conditions first order reactions are independent of pressure.

The majority of industrial organic processes are so complicated by the existence of side reactions, existence of more than one phase, consecutive reactions, reversible reactions, and complex compositions of the original reactants that they do not behave as first, second, or third order reactions. Hence, no wide use of mathematical formulations for predicting reaction rates has been made. Such equations that have been developed are empirical in origin and in general prove to be merely approximations applicable only over limited ranges of conditions. Complex systems, however, sometimes may be handled satisfactorily by methods of approximations analogous to those found satisfactory for simple cases.[14, 15] Even in cases where mathematical expression proves inadequate some information of a semi-quantitative nature can be predicted from the kinetics of similar reactions.

Effect of Temperature on Rate of Reaction—It is well known that temperature has a marked effect on the rate of reaction. For some time the statement that the rate of reaction is doubled by increasing the temperature 10 or 15° C. has been known to be inaccurate. In some cases it takes 50° C. or more to double the speed of a reaction. The most satisfactory mathematical relationship expressing the temperature effect on reaction velocity for a homogeneous system is the empirical equation developed by Arrhenius:

$$\frac{d(ln\, k)}{dT} = \frac{E}{RT^2}$$

which on integration gives:

$$ln\, k = \frac{-E}{RT} + C$$

where E = "energy of activation" per mol
k = reaction velocity constant at temperature T
R = the gas law constant
T = the absolute temperature
and C = a constant of integration.

In order to carry out the integration it was necessary to assume E to be constant. Since this assumption only holds for a limited temperature range, use of the Arrhenius equation should be restricted to temperatures in the neighborhood of those for which the values of E are known. From the integrated equation above it is evident that the limiting value of the reaction velocity constant, k, is determined by the value of C. This means that under conditions such that the quantity $\frac{E}{RT}$ is very small as compared to C, the rate of reaction is practically independent of temperature changes, which is in direct contradiction to the usual effect of temperature on reaction rate. These remarks should be sufficient to emphasize the necessity of making certain that the Arrhenius equation holds for the conditions under consideration before using it to predict the effect of temperature on reaction rate.

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[15] Kassel, L. S., "Kinetics of Homogeneous Gas Reactions." Reinhold Publishing Corp., New York. 1932.

For the majority of homogeneous reactions the Arrhenius equation is found to be relatively satisfactory over considerable changes of temperature. In our present state of knowledge the energy of activation E must be measured experimentally. Hence, if rate data are available at two different temperatures to permit E and C to be evaluated, it is possible to predict the velocity of a homogeneous reaction over the temperature range for which the equation holds.

The effect of temperature on the reaction rate of a homogeneous reaction is readily apparent from the integrated form of the Arrhenius equation. Since the reaction velocity constant, k, depends upon the difference between the values of C and $\frac{E}{RT}$, an increase in the value of T decreases the value of $\frac{E}{RT}$ which is subtracted from C, and hence the rate of reaction increases because the reaction velocity constant, k, increases in value.

The marked effect of temperature changes on reaction rates can be used to explain one of the difficulties encountered in carrying out exothermic reactions under adiabatic conditions. If a large quantity of heat is liberated by the reaction, the reaction mass will increase in temperature which in turn increases the reaction rate. If this continuous building up of the reaction rate is allowed to proceed unchecked the reaction will soon reach explosive violence. However, the equilibrium conversion decreases, for this type of reaction, with an increase in temperature and this tends to act as a safety valve by decreasing the amount of heat liberated due to the lower conversion. Hence, all exothermic reactions cannot be expected to reach explosive violence if carried out under adiabatic conditions, but this explanation should be sufficient to account for the necessity of controlling the temperature in many reactions.

In this discussion of rates of reaction no consideration has been given to the effect of reverse reactions, side reactions, successive reactions, temperature gradients and the like on the speed of reaction. Many cases of industrial importance are known in which it is not possible to neglect such effects. Other reactions are so complicated that a complete and rigorous analysis would be impracticable even though the basic theory were available. However, it should be emphasized again that in certain cases satisfactory methods of approximation have been developed whereby complex systems may be treated by relatively simple methods.[14, 16]

Heterogeneous Reactions—Heterogeneous reactions, particularly those involving catalysts, make up many of the most important industrial reactions of the present day. Unfortunately, on the basis of published data at least, it is impossible to make generalizations regarding the kinetics of such systems. The rates at which such reactions proceed is determined by a number of factors, such as type and condition of catalyst if present, rate of diffusion, type of reaction, character of reacting molecules, rate of heat transfer, etc., in addition to those already mentioned. Correlations based on unit processes have brought out certain qualitative factors regarding the reaction rates of such systems but the quantitative aspects are lacking. Much work has recently been done on this type of reaction, and it is hoped that an early release of such information will permit a quantitative treatment in the near future.

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[16] Sherman, J., Ind. and Eng. Chem., *28*, 1026-31 (1936).

All of these general principles have been known for some time, but few applications to industrial technology were made before the "unit processes" emphasized their wide applicability and utility. The limitations of our present knowledge of equilibria and reaction rates have become manifest and work is being carried out to bridge the gaps in our knowledge in this important field.

Function of the Pilot Plant—From a casual reading of the preceding discussion on equilibria and reaction rates one might conclude that such studies are interesting but of no practical value. Such a conclusion is far from the truth. The chemical industry spends millions of dollars annually for research in pilot plant equipment to obtain information on reaction rates and equilibrium conditions, as well as to test various arrangements of experimental equipment. In these studies, the fullest use of the available information is made in order to cut down the experimental work to a minimum. The principles just discussed are used as a basis for deciding what experimental work shall be done and in extrapolating and interpreting the data to get the most information from a minimum of experimental work. Though the equilibrium and kinetic considerations are not yet quantitative they are definitely not a waste of time as they serve as a framework for correlations which eventually will bring order out of chaos, just as similar work did for the unit operations.

THE ORGANIC UNIT PROCESSES

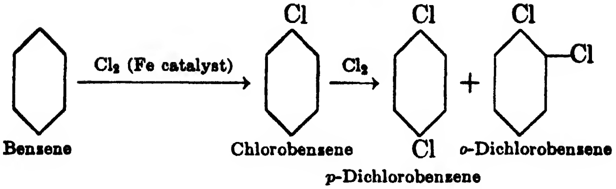
Since the unit processes are based on chemical reactions, unit process equipment is essentially apparatus in which the chemicals are brought together under the proper conditions and allowed to react. In many cases the equipment can be quite simple but in others it needs to be very elaborate with very careful control of operating conditions provided. For example, some reactions can be carried out in open vessels by simply mixing the materials together with very little heating or cooling. In other cases high-pressure equipment built of special corrosion-resistant materials and controlled by elaborate automatic devices is necessary. In this connection it should be pointed out that once the chemicals are brought together, the operator has no control over the chemical reactions that take place. All that he can do is to control the physical factors affecting the reaction so that the optimum yield of the desired product is obtained. Hence, the principal concerns of the equipment designer are to select the materials most suitable for the apparatus, and to get an arrangement of apparatus which will permit the necessary control of the principal factors affecting the reaction, such as temperature, pressure, concentration, time of contact, homogeneity of reaction mass, presence or absence of light or catalysts, etc. In the following pages a brief discussion of a number of organic unit processes is given. Applications of the fundamental principles already discussed are pointed out and the types of equipment used for the various unit processes are illustrated.

Halogenation—Halogenation may be defined as a process in which a halogen atom is introduced into an organic compound. Halogenation may occur by (1) addition; (2) substitution for an element; or (3) replacement of a group such as the hydroxyl or sulfonic acid group.

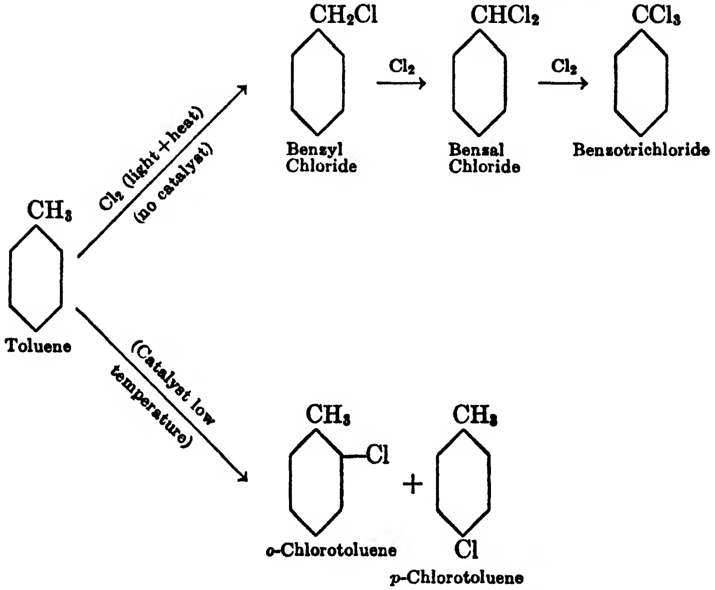
Examples:[17]

Substitution:

$$\underset{\text{Carbon Disulfide}}{CS_2} \xrightarrow[S]{Cl_2} \underset{\text{Carbon Tetrachloride}}{CCl_4}$$



(18)



(18)

$$\underset{\text{Pentane}}{C_5H_{12}} \xrightarrow{Cl_2} \underset{\text{Amyl Chloride}}{C_5H_{11}Cl} + HCl$$

Addition:

$$\underset{\text{Ethylene}}{H_2C{=\!=}CH_2} \xrightarrow{HOCl} \underset{\text{Ethylene Chlorhydrin}}{CH_2OH{-}CH_2Cl}$$

Replacement:

$$\underset{\text{Ethyl Alcohol}}{C_2H_5OH} \xrightarrow[FeCl_3]{HCl} \underset{\text{Ethyl Chloride}}{C_2H_5Cl} + H_2O$$

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[17] Because of the difficulty of adequately representing many of the organic reactions by a simple balanced equation, many of the equations used as illustrations in this chapter are not balanced but show only the principal reactants and products.

[18] The examples marked with this number were taken, with the author's permission, from Dr. Alexander Lowy's chapter on Industrial Organic Chemicals and Dye Intermediates published in the Fifth Edition of this Manual.

Organic halogen compounds are prepared by halogenation reactions on a large scale and are widely used industrially. Halogen derivatives are used to a considerable extent directly as cleaning fluids ($CHCl{=}CCl_2$, CCl_4); plant stimulants ($CH_2Cl \cdot CH_2Cl$); refrigerants (CF_2Cl_2, CH_3Cl); moth repellant and deodorant (p-Cl-C_6H_4-Cl); anesthetics ($CHCl_3$); general solvents (CCl_4); etc. The greater proportion of these compounds, however, is used as raw materials for a very large number of syntheses, e.g., in the preparation of alcohols, phenols, amines, alkylene oxides, ethers, dyes, acids, synthetic rubbers, hydrocarbons, alkaryl compounds, etc.[19] The importance of the unit process of halogenation is further emphasized by citing the fact that in 1936 the production of halogenated paraffins in the United States exceeded the total production of *all* aromatic compounds, including dyestuffs, by more than 110,000,000 pounds.

Of the halogen derivatives the chlorine compounds are the most important because they can be prepared cheaply. This discussion will deal almost exclusively with chlorine compounds, but it should be remembered that bromine, iodine, and fluorine derivatives have some advantages which make their use desirable in certain cases. The most important halogenation agents are as follows: Cl_2 (with or without catalyst), HCl, HOCl, SO_2Cl_2 $COCl_2$, PCl_5, Br_2, and I_2 and SbF_3.

Character of Reactions. Halogenation reactions are carried out in both liquid and vapor phases. Both thermal and catalytic reactions are employed. In the catalytic reactions, the halides of iron, antimony, phosphorus, and sulfur as well as actinic light serve as important catalysts. In the preparation of halogenated aromatic compounds, the catalysts not only speed up the reactions, but also influence the point at which the halogen enters the aromatic compound.

Hass and co-workers[20] have postulated a number of rules regarding the chlorination of paraffin hydrocarbons which should be of great value in predicting yields and rates of reaction in both liquid and vapor phase syntheses employing these materials.

Controlling Homogeneous Chlorinations. The reaction of chlorine with vapors of a paraffin hydrocarbon is exothermic and so vigorous in a homogeneous system that precautions must be taken to prevent it from reaching explosive violence.[21] Hence, numerous procedures have been devised to control the reaction rate and to avoid undesirable reactions which result in diminished yields. Such methods as the following are used:

1. Employing an excess of the hydrocarbon so that only a limited amount can react per cycle. The excess hydrocarbon is recovered and recycled.
2. Reacting the materials in the presence of a diluent gas, such as steam, nitrogen, or HCl.

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[19] For a discussion of the details of preparation and uses of a large number of chlorine derivatives see Chapters 13, 15 and 46. See also the discussion of the unit processes of amination by ammonolysis, hydrolysis, alkylation and condensation.

[20] Hass, H. B., and Marshall, J. R., Ind. and Eng. Chem., *23*, 352 (1931); Hass, H. B., McBee, E. T., and Weber, P., Ind. and Eng. Chem., *27*, 1190 (1935); *28*, 333 (1936); Hass, H. B., and Weber, P., Ind. Eng. Chem. Anal. Ed. 7, 231 (1935); Hass, H. B., McBee, E. T., and Hatch, L. F., Ind. and Eng. Chem., *29*, 1335 (1937). Summarized in Groggins, P. H., "Unit Processes in Organic Synthesis," McGraw-Hill Book Co., Inc., New York, 1938. pp. 165-171.

[21] See p. 101.

3. Reacting the hydrocarbon with a halogen gas that reacts mildly and then replacing the combined halogen with chlorine.
4. Employing a liquid solvent in which the hydrocarbon is soluble.
5. Carrying out the reaction in successive stages by mixing only part of the chlorine with the hydrocarbon and cooling between stages.
6. "Hot chlorination" of olefins; at temperatures above 500° C. the chlorine substitution reaction predominates over the addition reaction.[22]
7. Use of an excess of chlorine under high pressure.[23, 24] In this case the excess chlorine serves as the diluent gas and helps to keep the reaction temperature down.
8. Employing a molten salt bath in contact with the reagent.[25] The temperature of the bath can be maintained at the desired temperature by cooling and salts can be used which serve as catalysts for the desired reaction.

A study of the above methods shows that they are really applications of the Mass Action Law and the Le Chatelier Principle. For example, the use of a diluent gas, a liquid solvent, a molten salt bath, or an excess of hydrocarbon or chlorine assists in controlling the reaction temperature by increasing the heat capacity of the system and hence prevents large increases in temperature due to the exothermic reaction. In addition, the use of an excess of chlorine or hydrocarbon tends to increase the degree of completion of the reaction, while the use of a diluent decreases the reaction rate not only by making it more difficult for the reacting molecules to get together but also because the added heat capacity of the diluent tends to keep the temperature of the system down. In the case of the liquid solvent and molten salt bath, the inert material serves both as a diluent and as a medium for removing the heat of reaction.

Chlorination of Aliphatic Compounds. Because of the variety of products made by chlorinating aliphatic compounds, it is difficult to generalize on the conditions for chlorination of these materials. Reactions are carried out using both batch or continuous processes and reacting the materials in either liquid or vapor phase. The temperatures usually employed in liquid phase reactions range from about 30 to 200° C., and in vapor phase reactions from 200 to 500° C. Atmospheric or moderate pressures are commonly used but recent work indicates that high pressures may be desirable in certain cases.[24] The chlorination of aliphatic compounds other than hydrocarbons usually takes place at temperatures lower than are necessary for the paraffins.

The *chlorination of aromatic compounds* is generally carried out in the liquid phase, though the more volatile compounds are sometimes chlorinated in the vapor phase. Since chlorine may enter either the side chain or the ring, conditions must be properly selected in order to obtain the maximum yield of the desired compounds. In general, hot chlorination in the absence of a catalyst

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[22] Groll, H. P. A., and Hearne, G., Ind. and Eng. Chem., *31*, 1530-7 (1939).

[23] McBee, E. T., Hass, H. B., and Pierson, E., Ind. and Eng. Chem., *33*, 181-5 (1941).

[24] McBee, E. T., Hass, H. B., and Pianfetti, J. A., Ind. and Eng. Chem., *33*, 185-88 (1941).

[25] McBee, E. T., and Haas, H. B., Ind. and Eng. Chem., *33*, 137-42 (1941). Especially pp. 138-39.

favors introduction of chlorine in the side chain, while chlorination at a lower temperature in the presence of a catalyst, such as iron, favors the replacement of nuclear hydrogen.[26] In certain halogenations, because of the orienting influence of groups already present, it is necessary to employ two or more chlorination methods to get the desired chlorine compound. In the chlorination of aromatic materials which are normally solids at ordinary temperatures it is frequently necessary to employ solvents. Inert solvents, or solvents such as benzene and nitrobenzene, which ordinarily react readily with chlorine, can be used in cases where chlorine reacts much more readily with the solute than with the solvent.

Apparatus for Chlorination. The conditions for carrying out halogenations vary so widely that no general rules for the design and construction of equipment can be formulated. For example, chlorinations are carried out in jacketed vessels, in packed towers, in molten salt baths, and in tubular equipment. Both continuous and batch processes are used. Due to the corrosive action of the reagents and the acids formed by the reactions, the materials of construction must be carefully selected. With non-aqueous media, the usual materials are iron, alloys, copper, or lead though vitreous silica,[27] glass or glass-lined equipment may be utilized. Tantalum seems to be the best material for use when both H_2O and HCl are present, but because of cost its use is limited. Lead-lined steel reactors are used where aqueous HCl may be present and lead coils are used for temperature control.

In addition to corrosion resistance, chlorination equipment should have the following features: (1) Provision must be made for dissipating the heat of reaction. In liquid phase reactions carried out in autoclaves, this is usually accomplished by circulating a cooling medium through the jacket of the chlorinator, or through coils suspended in the reaction vessel. (2) Agitation must be provided for heterogeneous systems. This may be accomplished by outside circulation with a pump or by providing a mechanical stirrer in the reaction mass. (3) Provision must be made for getting the reacting materials into the chlorinator and for removing the products of the reaction. (4) Careful control of the concentrations must be provided in order to prevent undesirable side reactions and explosions. (5) Sight glasses should be provided for observation of the reaction and to detect the escape of unreacted chlorine. In case the reaction is photocatalytic, provision should be made for exposing the reaction mass to light. A variety of methods have been developed for commercial chlorinations embodying these features.[28]

Hydrolysis (including alkali fusion)—Hydrolysis may be defined as a process in which a double decomposition reaction is carried out with water as one of the reactants. In this discussion the meaning of the term has been extended to cover also the alkali fusion reactions which are very similar to hydrolysis reactions. This process is used principally for the conversion of —X to —OH;

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[26] See Example 3, Chlorination of Toluene, p. 103.

[27] Winship, W. W., Ind. and Eng. Chem., *33*, 143-148 (1941).

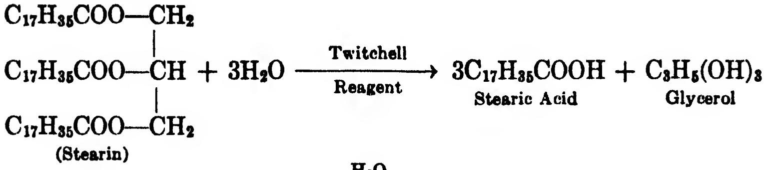
[28] See Groggins, P. H., "Unit Processes in Organic Synthesis," 2nd. ed., McGraw-Hill Book Co., Inc., New York, 1938. Especially pp. 174-231.

ester to alcohol and acid or alcohol and soap; —CN to —$CONH_2$ to —COOH; —OSO_2H to —OH; and for cleavage of C—C linkages in large molecules, such as those of proteins and carbohydrates.

Examples:

$$\underset{\text{Ethylene Chlorhydrin}}{CH_2OH \cdot CH_2Cl} \xrightarrow{H_2O} \underset{\text{Ethylene Glycol}}{CH_2OH \cdot CH_2OH}$$

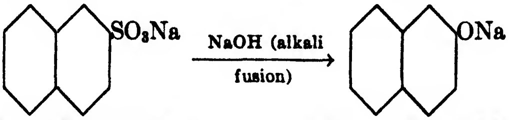
$$\underset{\text{Starch}}{(C_6H_{10}O_5)x} + xH_2O \xrightarrow[H_2O]{HCl} \underset{\text{Glucose}}{xC_6H_{12}O_6}$$



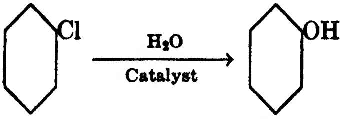
$$\underset{\text{(Stearin)}}{\begin{array}{l} C_{17}H_{35}COO—CH_2 \\ C_{17}H_{35}COO—CH \\ C_{17}H_{35}COO—CH_2 \end{array}} + 3H_2O \xrightarrow[\text{Reagent}]{\text{Twitchell}} \underset{\text{Stearic Acid}}{3C_{17}H_{35}COOH} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}$$

$$\underset{\text{Amyl Chloride}}{C_5H_{11}Cl} \xrightarrow[NaOH]{H_2O} \underset{\text{Amyl Alcohol}}{C_5H_{11}OH}$$

$$\underset{\text{Ethyl Sulfuric Acid}}{CH_3—CH_2OSO_3H} + H_2O \longrightarrow \underset{\text{Ethyl Alcohol}}{CH_3—CH_2OH} + H_2SO_4$$



Sodium Naphthalene-2 Sulfonate Sodium β-Naphtholate



Chlorobenzene Phenol

Uses of Hydrolysis. Hydrolysis reactions are widely employed for splitting fats and oils to form glycerol and fatty acids or soaps.[29, 30] All carbohydrates, including sugars, cellulose, starch, and other polysaccharides can be hydrolyzed. The hydrolysis of starch is the basis of a large industry.[31] Corn sirup for confectionery trade or table use and corn sugar (glucose) are the principal products from the hydrolysis of corn starch. In Europe the hydrolysis of wood cellulose to glucose is being carried out on an industrial scale.[32] Two processes have been reported, one employing dilute sulfuric acid (0.2 to 0.1% by weight) and the other fuming hydrochloric acid as the hydrolysis reagent. The hydrolysis of organic halides and alkyl esters of sulfuric acid (prepared from unsaturated hydrocarbons and sulfuric acid) are widely used methods for the preparation of alcohols and phenols such as amyl alcohol, ethyl alcohol, ethylene glycol, iso-

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[29] The preparation of soaps from fats or oils with an alkali solution is usually called "saponification."

[30] For details of preparation and uses see Chapters 32 and 42.

[31] See Chapter 36.

[32] Bergius, F., Ind. and Eng. Chem., *29,* 247-53 (1937).

propyl alcohol, and phenol. The latter material is in great demand for use in plastics.[33]

Conditions for Hydrolysis. In practically all cases of industrial importance hydrolysis reactions are carried out in the presence of either acids or bases as catalysts. Dilute hydrochloric acid and sulfuric acid are the most commonly used acids and caustic soda, sodium carbonate, and sodium bicarbonate are the most common alkalies used. Enzymes are used as catalysts for hydrolysis reactions in the brewing industry.

Most hydrolysis reactions are carried out in the liquid phase and the temperatures are usually in the range of 80 to 220° C. The pressures used vary from one to 200 atmospheres. Though the use of a high temperature may affect the equilibrium point adversely, in commercial practice the highest temperature practicable is employed in order to complete the reaction in the minimum time. Several methods of increasing the rate of hydrolysis are worthy of mention. Since many of the organic compounds which are hydrolyzed are insoluble in water, efficient agitation, by means of an agitator or recirculation by means of a pump, in conjunction with an emulsifying agent markedly increases the rate of hydrolysis. Other methods include pressure percolation followed by immediate cooling (wood hydrolysis), carrying out the reaction in successive stages with removal of part of the products between stages (soap making), and recirculation of an equilibrium mixture of by-products to prevent further formation of these materials (recirculation of diphenyl oxide in the preparation of phenol). Though increasing the concentration of hydrolyzing reagent tends to increase the rate of reaction, in several cases it has been found that such high concentrations result in undesirable by-products and are therefore avoided in these instances.

Vapor-phase hydrolysis reactions and alkali fusions are carried out at temperatures ranging from 300 to 500° C. Only a few vapor phase hydrolytic reactions are used commercially, while alkali fusion is limited essentially to the replacement of $—SO_3H$ by OH.

Hydrolysis Equipment. In the matter of equipment design, alkaline processes in general have the great advantage over acidic processes since they can usually be carried out in steel or iron reaction vessels. Such vessels are simple in design, usually requiring only some method for heating and agitating the reaction mass. Even the severe conditions of caustic fusion do not seem to greatly shorten the life of cast iron pots in which they are carried out. Both batch and continuous processes are used.

Acid processes, on the other hand, present a difficult problem in equipment design. Duriron or lead-lined equipment is necessary for processes in which sulfuric acid is used. In addition to the lead-lining, acid-resisting brick or Pyrex glass brick can be employed for additional protection. With hydrochloric acid, corrosion is even more severe unless the reaction is carried out with dilute acid (less than 1% HCl by weight) and at low temperatures, in which cases bronze and copper suffice. For higher concentrations, especially at higher temperatures, stoneware, or iron, lined with an acid-resisting tile joined with a special cement, is necessary. Rubber-lined iron is used to some extent and tantalum is finding favor in continuous large-scale processes where HCl is used as the catalyst.

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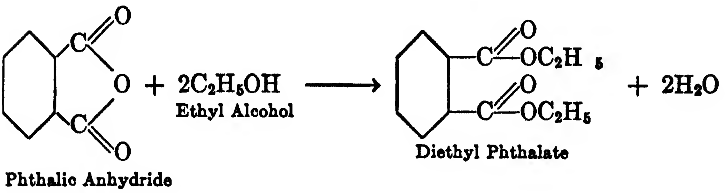
[33] See Chapter 31.

Esterification—The process of preparing an ester is called "esterification." Esters of organic acids can be represented by the general type formula RCOOR′, when R and R′ represent hydrocarbon or substituted hydrocarbon radicals. Esters of inorganic acids can be represented by the formula ROA′, where R represents a hydrocarbon or substituted hydrocarbon radical and —OA′ represents an inorganic acid radical (such as $—ONO_2$, $—OSO_3H$, etc.). A variety of reagents can be used for the preparation of esters but the usual reagents are alcohols or phenols with acids or their anhydrides in the presence of dehydrating agents (HCl, H_2SO_4, etc.).

Examples:

$$\underset{\text{Acetic Acid}}{CH_3COOH} + \underset{\text{Butyl Alcohol}}{C_4H_9OH} \longrightarrow \underset{\text{Butyl Acetate}}{CH_3COOC_4H_9} + H_2O$$



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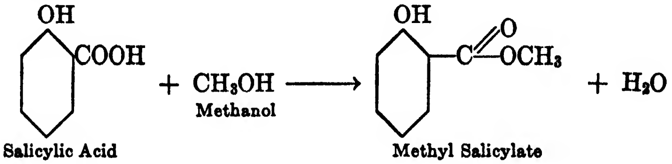
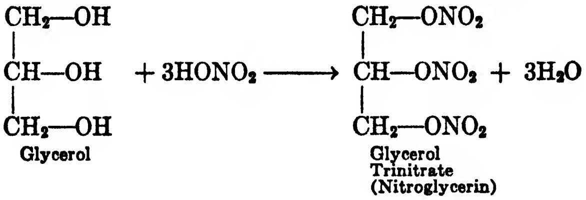


$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2SO_4 \longrightarrow \underset{\text{Ethyl Sulfuric Acid}}{CH_3—CH_2OSO_3H}$$



$$\underset{\text{Glycerol}}{\begin{array}{l} CH_2—OH \\ | \\ CH—OH \\ | \\ CH_2—OH \end{array}} + 3HONO_2 \longrightarrow \underset{\substack{\text{Glycerol} \\ \text{Trinitrate} \\ \text{(Nitroglycerin)}}}{\begin{array}{l} CH_2—ONO_2 \\ | \\ CH—ONO_2 \\ | \\ CH_2—ONO_2 \end{array}} + 3H_2O$$

$$\underset{\text{Ketene}}{CH_2{=}CO} + \underset{\text{Ethyl Alcohol}}{C_2H_5OH} \longrightarrow \underset{\text{Ethyl Acetate}}{CH_3COOC_2H_5}$$

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_y} + \underset{\text{Acetic Anhydride}}{3y(CH_3CO)_2O} \xrightarrow{H_2SO_4} \underset{\text{Cellulose Acetate}}{[C_6H_7O_2(CH_3COO)_3]_y} + \underset{\text{Acetic Acid}}{3y\ CH_3COOH}$$

Esters have several important properties which make them of great value as industrial chemicals. Large quantities of acetates, such as butyl acetate, ethyl acetate, amyl acetate, are used as solvents, especially in the lacquer industry.[34] Because of their pleasant odor and taste quite a large number of esters find use in perfumes, flavors, and perfumed soaps. Several of the esters have valuable plasticizing properties, e.g., dibutyl phthalate and diethyl phthalate.[35] Esters of nitric

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[34] See Chapter 30.
[35] See Chapter 31.

acid, such as glycerol trinitrate, glycol dinitrate, and cellulose nitrate, have valuable explosive properties.[36] Cellulose nitrate (called nitrocellulose) and cellulose acetate are valuable as plastics, while the latter is also used in large quantities as synthetic fabrics.[37]

The *operating conditions* for industrial esterification reactions are mild in comparison with most of the other unit processes. The temperatures range from about 10 to 200° C. Atmospheric pressure or slightly above is commonly used. Though an increased temperature speeds up esterification, the use of this method for the volatile esters makes it necessary to use pressure vessels. Fortunately, by the use of catalysts, esterification reactions can be carried out in a reasonable time at relatively low temperatures, and this is the method employed industrially. Sulfuric acid and hydrochloric acid are the most common catalysts used. Esterification reactions are reversible and the equilibrium conditions are such that a considerable proportion of the original reactants are present when equilibrium is established. Hence, it is usually necessary to employ some method to increase the degree of completion of the desired reaction. The following methods have been used successfully: continuous removal by distillation of water or ester as it is formed in the reaction; passing a gas slowly through the reaction mass to remove H_2O; addition of liquids, such as benzene, ethylene chloride, and carbon tetrachloride to assist in bringing over the water in a constant-boiling mixture.

Equipment for Esterification. The simple esters are prepared in standard distillation apparatus, the ester being formed either in the still body or in the fractionating column itself. Copper apparatus is generally used for this type of esterification. Both batch and continuous processes are employed. Illustrations of esterification equipment may be found in other chapters of this book.[38, 39]

Nitration—Nitration is the process by which the union of the $—NO_2$ group directly to a carbon atom is effected. In organic nitro compounds the nitrogen in the $—NO_2$ group is united directly to a carbon atom. In organic nitrates the nitrogen of the $—NO_2$ group is united to a carbon by means of an intermediate oxygen atom. The organic nitrates are really esters of nitric acid and they are discussed under the unit process of esterification.[40]

In most cases nitration is carried out by the use of mixed acids; for example, HNO_3 admixed with a dehydrating agent, such as oleum, sulfuric acid, acetic anhydride, or acetic acid. Other nitrating agents are HNO_3 alone, $NaNO_3 + H_2SO_4$, N_2O_4, nitrosulfonic acid (HSO_3NO_2) and organic nitrates, such as acetyl and benzoyl nitrate.

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[36] See Chapter 32.

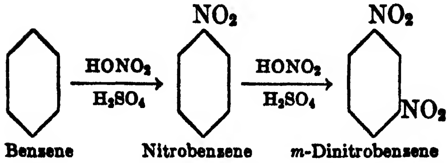
[37] See Chapters 38, 32 and 31.

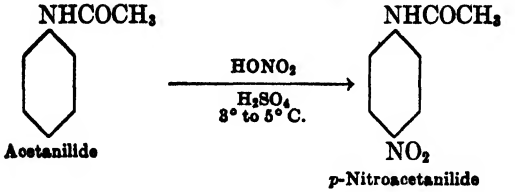
[38] See Chapter 2 for illustrations of distillation apparatus.

[39] See Chapters 38, 32 and 30.

[40] See p. 109.

Examples:





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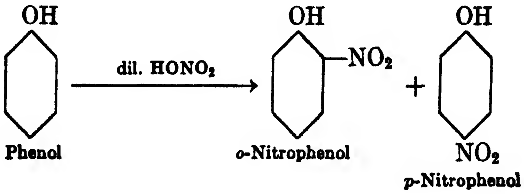

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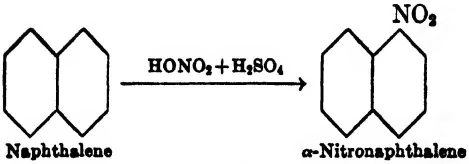

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$$\underset{\text{Propane}}{C_3H_8} \xrightarrow[\text{Vapor Phase}]{HONO_2} \text{1 nitropropane, 2 nitropropane, nitromethane, nitroethane.}$$

Uses of Nitro Compounds. The nitro compounds prepared by nitration reactions are used principally as intermediates for organic syntheses, dye manufacture, and for explosives. Nitrobenzene, dinitrobenzene, nitronaphthalene, dinitrochlorobenzene, *p*-nitrotoluene-*o*-sulfonic acid, and *m*-nitro-*p*-toluidine are some of the important nitro compounds.

Nitration of an aromatic compound is usually a liquid phase reaction in which a mixture of nitric acid and sulfuric acid is the nitrating agent. The concentration of both the nitric acid and sulfuric acid, as well as the proportion of mixed acid to compound being nitrated, are important variables to consider when nitration conditions are chosen. Since the nitration reaction is highly exothermic, some method of controlling the temperature must be provided to prevent the formation of undesirable oxidation products and to keep the reaction from reaching explosive violence. Nitration temperatures range from 0 to about 90° C., with temperatures in the neighborhood of 40 to 50° C. being commonly used. Nitrators usually have internal cooling coils to remove the heat of reaction and keep the temperature at the desired level. Agitation is also provided to avoid local super-heating, to prevent the formation of more highly nitrated products, and to increase the speed of the reaction.

Nitration of Paraffins. Though long thought to be impossible, methods of nitrating paraffin hydrocarbons with nitric acid at high temperatures have been discovered and already commercial developments are under way.[41] The nitroparaffins are excellent solvents for many of the synthetic resins such as cellulose acetate, cellulose nitrate, and vinylite.[42] In addition, they are quite reactive chemically and may soon become important as intermediates in the preparation of chemicals. In contrast to the low temperatures and high acid concentrations used for the preparation of aromatic nitro compounds, nitrations of paraffin hydrocarbons are carried out at higher temperatures (130 to 140° C.) with relatively dilute acids. Vapor phase nitrations are performed at much higher temperatures (390 to 450° C.). An excess of hydrocarbon is employed to prevent explosions, and the reactions are performed in stainless steel tubular apparatus.

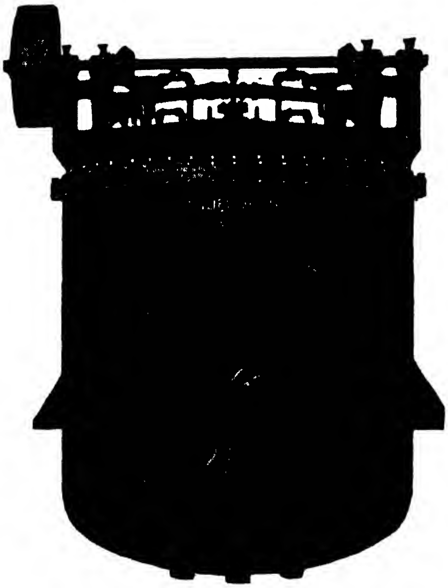

FIG. 1. Cast Iron Nitrator.

Although continuous *nitration apparatus* has been developed, batch processes are used in most cases. Fig. 1 shows a jacketed cylindrical type of nitrator equipped with internal acid-resisting iron cooling tubes and a marine type propeller for agitation. The cooling tubes are of the closed end type and are designed for close temperature control by circulating brine or cold water. The propeller operates in a draft tube, with vanes arranged to counteract swirl, and provides positive agitation and circulation. The bottom of the nitrator slopes to a sump to permit complete discharge through the blow pipe. The outside cooling jacket is of welded steel construction. Connections for installing temperature indicating devices are provided so that the operator can keep a close check on the temperature of the reaction mass at all times.

Amination by Reduction—Amination is a process in which an amine is formed by the production of the linkage $-\overset{|}{\underset{|}{C}}-NH_2$. Two methods of amination are commonly used: namely, amination by reduction, and amination by ammonolysis. Amination by reduction of nitro compounds is the usual method employed in the industrial preparation of aromatic amines, while ammonolysis is commonly used for the preparation of aliphatic amines and can be used for

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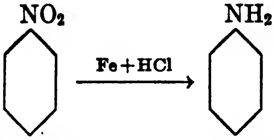
[41] McCleary, R. F., and Degering, E. F., Ind. and Eng. Chem., *30,* 64 (1938); Hass, H. B., and Hodge, U. S. 1,969,667 (1934); U. S. 2,071,122 (1937); Hass, H. B., and Patterson, J. A., Ind. and Eng. Chem., *30,* 67 (1938). Gabriel, C. L., Ind. and Eng. Chem., *32,* 887-92 (1940).

[42] See Chapter 30.

aromatic amines. Amination by reduction will be discussed in this section and amination by ammonolysis in the next section.[43]

The discussion of amination by reduction is limited to the reduction of nitro compounds. Many reducing agents are resorted to under variable conditions. The following are used industrially: Fe and HCl; tin and zinc with acids, or alkali or metal sulfides, such as Na_2S and $(NH_4)_2S$, in solution or suspension; gaseous hydrogen or CO; $FeSO_4$; $Na_2S_2O_4$; and Fe or Zn in alkaline solution.

Examples:



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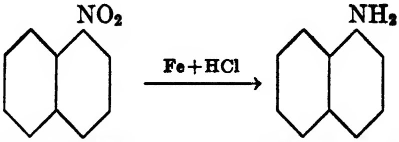
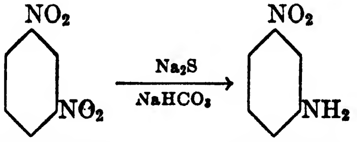
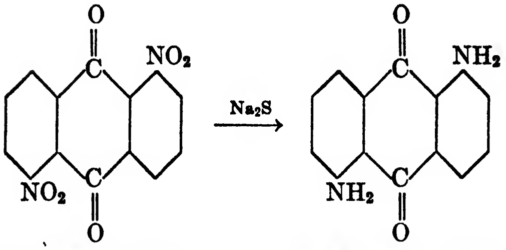
Nitrobenzene Aniline



α-Nitronaphthalene α-Naphthylamine



m-Dinitrobenzene m-Nitroaniline



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1,5 Dinitroanthraquinone 1,5 Diaminoanthraquinone

Aromatic amines are used principally for the preparation of synthetic organic chemicals and dye intermediates[44] but they also find some use as solvents, emulsifying agents, insecticides, rubber accelerators, antiseptics, and medicinals.

Conditions for Reduction. In technical aminations nascent hydrogen is commonly produced from the reaction of finely divided iron with dilute hydrochloric acid. The reactions are carried out at the boiling point of the solution at atmospheric pressure. The iron not only provides active hydrogen by reacting with the acid present but also furnishes the metal adsorption surface for the reaction. It also enters into the reaction by regeneration of ferrous chloride (catalyst) and acts as an oxygen carrier. Hence, it is necessary to use a finely divided iron and

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[43] See p. 114.

[44] See Chapter 28.

to keep it thoroughly mixed with the rest of the reaction mass. This requires the use of efficient, sturdy agitators. Sleeve and propeller or double-impeller type agitators have been found satisfactory for this purpose. As the reaction is distinctly exothermic, the heat of reaction is sufficient to maintain the material at the reaction temperature as long as iron is being added. Most reducers are steam jacketed, however, in order to permit the charge to be heated initially, and to supply the necessary heat to complete the reaction after all of the iron has been added. This procedure results in considerable saving in overall time required for the reaction.

Equipment for Reduction. Figure 2 shows a 1600-gallon cast iron jacketed reducer. The cast iron jacket is integral with the side wall and covers the lower part of the body. This jacketing permits very uniform heating of the areas adjacent to the reactants and prevents dilution due to the introduction of live steam into the reducer when heating is necessary. This reducer is equipped with cast iron liner plates to protect the body against abrasive action of the iron borings in the reducer charge. These removable liners may be taken out and replaced through the door on the side. The charge and sludge can be removed from the reducer by a quick-acting valve faced with a wooden plug. A plow type of rabble is used in the above reducer. This type of rabble is necessary to lift the heavy iron borings from the bottom of the reducer to give a homogeneous reaction mass. A simple form of lifting device is also provided which permits raising the rabble out of the sludge in an emergency or for cleaning.

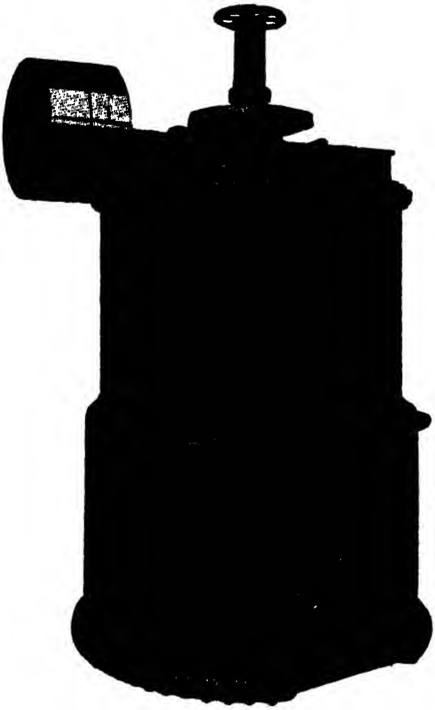
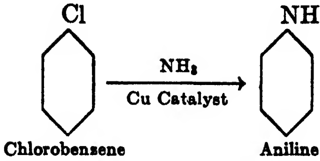


FIG. 2. Jacketed Cast Iron Reducer. (Courtesy Bethlehem Foundry & Machine Co.)

Amination by Ammonolysis—Amination by ammonolysis refers to those reactions wherein an amino compound is formed as a result of the action of ammonia. This process is utilized mainly for the substitution of the —Cl, —OH, and —SO_3H groups by the —NH_2 group, but some reactions involving simple addition and the replacement of oxygen are also of industrial importance:

Examples:



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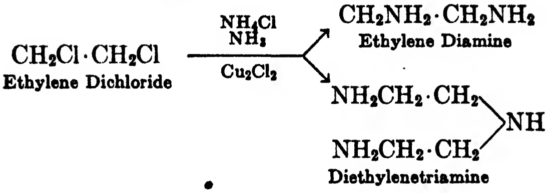
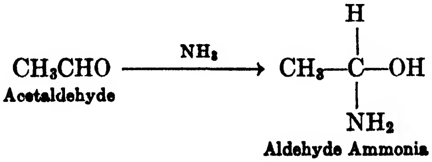
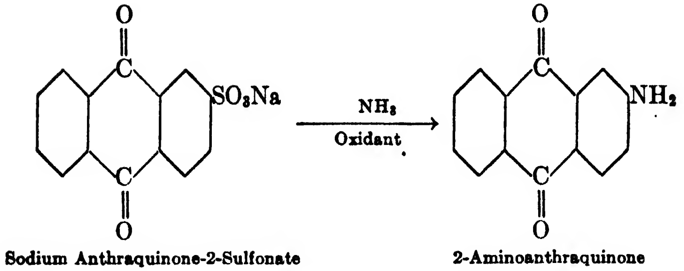




$$CH_3CHO \xrightarrow{NH_3} CH_3-\overset{\displaystyle H}{\underset{\displaystyle NH_2}{C}}-OH$$



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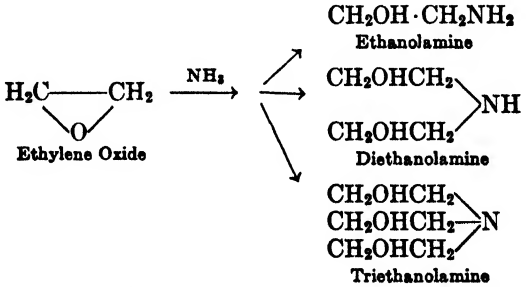

Conditions for Ammonolysis. Though the great majority of aminations are carried out in the liquid phase using aqueous ammonia, anhydrous ammonia can be used, and the ammonolysis of alcohols, oxides, and aldehydes may often be carried out most advantageously in the vapor phase. Ammonolysis reactions are usually carried out at temperatures ranging from about 165 to 210° C. With the solutions ordinarily used this requires pressures of 500 to 950 lb. per square inch, but in some cases pressures as high as 3,000 pounds per square inch are employed.[45] If the compound being aminated is insoluble in aqueous ammonia,

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[45] See Chapter 4 for a discussion of high pressure equipment.

it is necessary to provide efficient agitation to create a homogeneous reaction mass. In agreement with Le Chatelier's principle, the use of a high ratio of concentrated ammonia to compound being aminated promotes ammonolysis. Because of the high vapor pressure of ammonia at the amination temperatures commonly used, it is necessary to limit the free space above the solution. (See Figure 3.) If this is not done, enough ammonia will enter this vapor space to materially reduce the concentration of ammonia in the liquid, thereby decreasing the rate of reaction. Copper and copper salts are particularly effective as catalysts for ammonolysis reactions.

Apparatus for Ammonolysis. Since ammonolysis reactions are carried out at elevated temperatures and pressures, either high pressure autoclaves or tubular reaction equipment must be used. Autoclaves are used for batch processes and tubular equipment for continuous processes. Jacketed, steam-heated vessels are used up to temperatures of about 190° C. When higher temperatures are necessary oil or hot water under pressure is the customary heating fluid. It is usually necessary to provide for mechanical agitation if autoclaves are used for the reaction. Horizontal vessels, provided with a number of rotating splash arms, are preferred in the ammonolysis of compounds difficult to wet out and which are converted only at high temperatures. Figure 3 shows a 650-gallon autoclave of this type built for a working pressure of 1000 pounds per square inch. Figure 4 is a cross sectional drawing of a vertical high pressure autoclave. This autoclave is fitted with a turbine type agitator and is jacketed to permit the reaction mass to be heated.

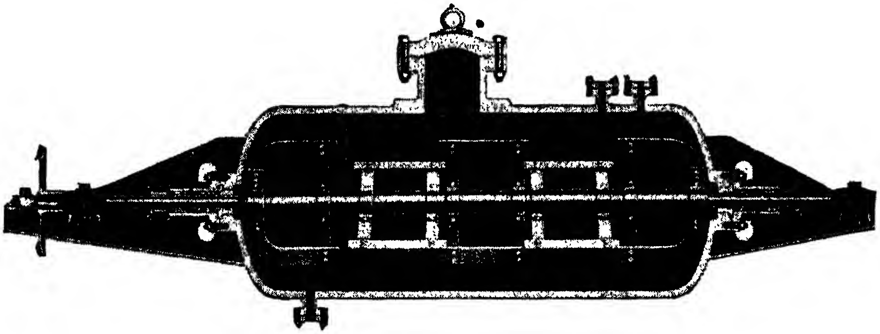
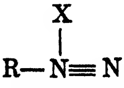


FIG. 3. Horizontal High Pressure Autoclave. (Courtesy Blaw-Knox Co.)

Diazotization and Coupling—Diazotization is the process by which a diazo or diazonium compound is prepared. Diazotization involves the reaction between a primary aromatic amine and nitrous acid. Both diazo and diazonium compounds may be formed simultaneously. Diazo compounds have the structure R—N=N—X, while diazonium compounds have the structure  $R{-}\overset{\overset{\displaystyle X}{|}}{N}{\equiv}N$. Coupling is the process by which a diazo- or diazonium compound is united with coupling compounds such as aromatic amines and phenols. The two unit processes are discussed together because of their similarity. Diazotization is usually an intermediate step in the preparation of azo dyes in which coupling is the final step, and because of their instability the diazonium or diazo compounds are usually not separated as such from the solution in which they are prepared. Diazotization can be employed for the preparation of organic compounds not readily prepared by other means.

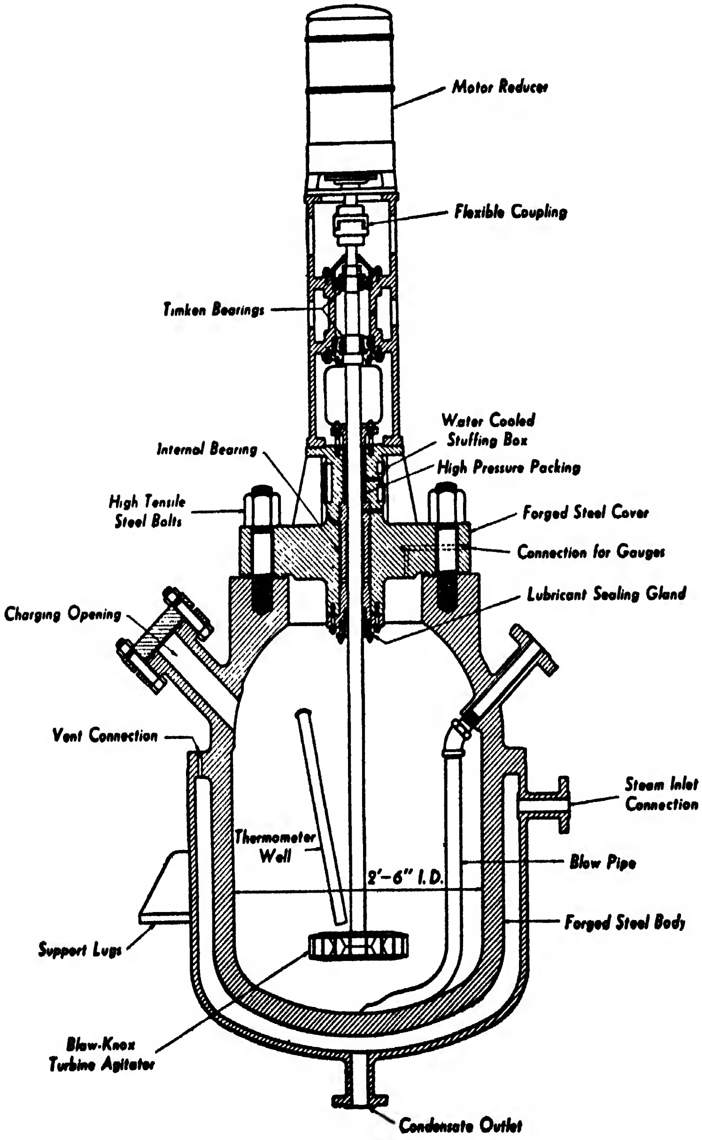
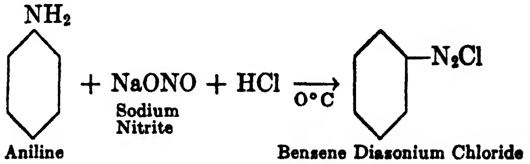
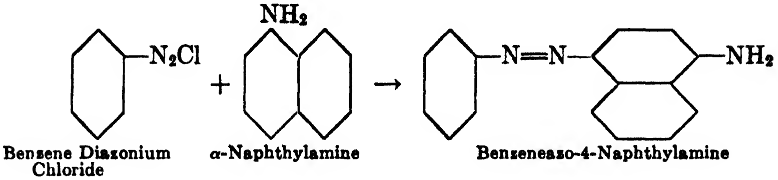


FIG. 4. Vertical High Pressure Autoclave. (Courtesy Blaw-Knox Co.)

Example of diazotization reaction:



Example of coupling reaction:



Conditions for Diazotization.[46] Technical diazotizations are usually carried out under mild conditions in aqueous acid solutions in which amines are soluble. With the usual concentrations employed, the reactions are so rapid, even at low temperatures, that most diazotizations are completed in from 5 to 60 minutes. Low temperatures, between 0 and 20° C., are used to avoid undesirable reactions of the diazonium salts. Because of the mild reaction conditions, the speed of the reaction, and the quantities of material made, the equipment used for technical diazotizations is relatively simple. The reaction vessels usually consist of tubs or tanks provided with agitation. The materials of construction used must not reduce the diazo compounds and must withstand the dilute acids used. Wooden tubs, tile-lined iron tanks, stoneware, rubber, enamel-lined iron, and lead are suitable materials. Lead is ordinarily the only metal used in direct contact with diazonium salts, but some diazotizations are carried out in concentrated sulfuric acid solutions in iron reaction vessels.

Coupling [47] represents the last step in the preparation of azo dyes from diazonium salts. Coupling reactions may be used to form solid dyes, or for the formation of the dye directly on the cloth. The reaction conditions are similar to those of diazotization with respect to temperature, time, and concentrations as well as types of equipment.

The azo dyes formed by diazotization and coupling are used not only to color textiles but also a wide variety of other materials such as inks, paints, gasoline, and solvents.[48]

Oxidation—Oxidation may be defined as the process whereby oxygen is introduced into, or hydrogen removed from an organic compound by means of an oxidizing agent. The following oxidizing agents are used: Air, O_2, $KMnO_4$, $K_2Cr_2O_7$ + Acid, $KClO_3$, NaOCl, PbO_2, H_2O_2, HNO_3, Ferric salts, etc.

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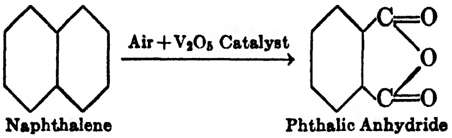
[46] See Chapter 28.

[47] See Chapters 28 and 29.

[48] See Chapter 29.

Examples:

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{\text{Air + Cu Catalyst}} \underset{\text{Formaldehyde}}{HCHO} \qquad (18)$$



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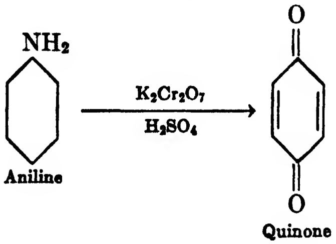
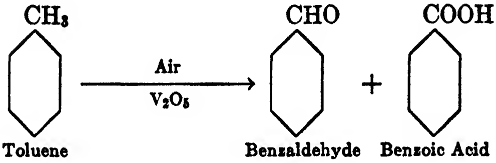
$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{Catalyst}]{\text{Air}} \underset{\text{Acetic Acid}}{CH_3COOH} \qquad (18)$$





Oxidation reactions constitute one of the most powerful means of synthesizing organic chemicals. Complete oxidation, however, results in the formation of carbon dioxide and water, which usually are less valuable than the original substances. Complete oxidation is likely to occur unless the proper precautions are observed, but if the reaction can be controlled so that only partial oxidations occurs, valuable chemicals are frequently obtained. Formaldehyde,[49] acetic acid, phthalic anhydride,[50] camphor, vanillin, benzaldehyde, benzoic acid, alizarin,[51] anthraquinone,[51] and indigo[51] are a few of the many important compounds prepared by oxidation reactions.

There is a *marked difference in the behavior of aromatic and aliphatic hydrocarbons* with regard to oxidation. Aromatic hydrocarbons are fairly resistant to oxidation and, in general, the reactions are carried out at elevated temperatures employing an active catalyst and an excess of oxidizing agent. There seem to be points of resistance where it is relatively simple to stop the oxidation at an intermediate stage. Naphthalene to phthalic anhydride is an example. See example 2. Aliphatic hydrocarbons, on the other hand, are easily oxidized and there are apparently no real points of resistance to oxidation in these compounds. This makes it necessary to control the temperature carefully and use only limited amounts of oxidizing agent when these materials are oxidized. Even then there

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[49] See Chapter 30.

[50] See Chapter 31.

[51] See Chapter 28.

is a marked tendency to form complex mixtures which are difficult to separate into pure compounds.

Control of Partial Oxidation. Oxidation reactions of organic compounds are exothermic, and are accompanied by a decrease in free energy. Hence, equilibrium is favorable, and usually it is necessary to take steps to limit the extent of the reaction rather than force it to completion. No matter how favorable the equilibrium may be, suitable reaction rates must be obtained before useful processes are possible. The methods that have been used to provide these favorable rates and for limiting the extent of oxidation have resulted in the great variety of organic oxidation reactions now in use.

Conditions for Oxidation. Both liquid-phase and vapor-phase oxidation methods are successfully utilized. Liquid-phase reactions are employed in cases where high molecular weight, complex, thermally unstable substances are dealt with, and where the oxidizing agent is relatively nonvolatile. The preparation of vanillin, camphor, quinone, alizarin, fatty acids from petroleum, and acetic acid are examples. This type of reaction is conducted at low or moderate temperatures, and the extent of oxidation may be readily controlled by (1) limiting the time of contact with oxidizing agent; (2) controlling the temperature; (3) limiting the amount of oxidizing agent; and (4) varying the type of oxidizing agent used.

Vapor-phase oxidation may be applied to materials readily vaporized which do not decompose at the elevated temperatures employed. The preparation of methanol, maleic acid, and phthalic anhydride are examples. The products of oxidation must be thermally stable and fairly resistant to further oxidation before this type of oxidation can be used. Solid or vapor-phase catalysts can be successfully employed to assist in obtaining the desired reaction. The temperatures are usually high. A short time of contact, low oxygen concentrations, selective catalysts, and low conversions per pass are necessary to obtain reasonable yields of the product.

Since most oxidation reactions are highly exothermic, some means must be provided for removing heat fast enough to prevent the temperature from rising to a point where complete oxidation takes place. In liquid-phase reactions the temperature can be controlled by the rate of addition of oxidizing agent, by removal of heat in the form of latent heat, by cooling and recirculating part of the reaction mass, or by use of a cooling medium circulated through jacketed vessels or cooling coils. Since the temperatures are usually low, and the rate of heat generation under close control, these methods usually suffice. With vapor-phase reactions, however, rather severe conditions are encountered and more elaborate methods must be used for temperature control. These reactions may be carried out in tubular equipment which has a relatively high ratio of heat transfer surface to volume of reacting materials. The use of a catalyst that is a good heat conductor with a tube that is relatively "black" which enables more heat to be transmitted to the tube wall by radiation seems to be of value in controlling the reaction temperature. The removal of heat from the outer surface of the tube may be accomplished by the use of boiling liquids such as mercury, sulfur, and diphenyloxide. These materials not only have high heat capacities and low resistance to heat flow, but also permit accurate control of the temperature merely by controlling the pressure.

The *equipment* used for oxidation reactions may be simple or very elaborate. Liquid phase reactions may be carried out in closed jacketed kettles provided with suitable means for regulating the rate of flow of reactants and products. Apparatus for vapor-phase oxidations must be more elaborate than for liquid-phase reactions. Most organic compounds are sensitive to heat and have a tendency to decompose even though they are not oxidized. This means that it is essential to bring the substance to the reaction temperature in the minimum of time. The difficulty of controlling the temperature at the desired level has already been mentioned. Finally, to avoid further oxidation or decomposition, the reaction products must be cooled immediately after leaving the reaction zone. Many modifications of reactors are available for the oxidation of organic compounds.[52]

Hydrogenation—Hydrogenation may be defined as a process in which gaseous hydrogen is caused to react with an organic compound by addition, substitution, or molecular cleavage (hydrogenolysis).

Examples:

a. Reduction of C=O

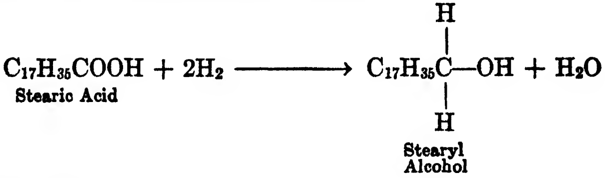
$$\underset{\text{Carbon Monoxide}}{CO} + 2H_2 \xrightarrow[\text{High Press.}]{\text{Catalyst}} \underset{\text{Methanol}}{CH_3OH}$$

b. Addition to a double bond

$$\underset{\text{Olein}}{(C_{17}H_{33}COO)_3\ C_3H_5} + 3H_2 \longrightarrow \underset{\text{Stearin}}{(C_{17}H_{35}COO)_3C_3H_5}$$

$$\underset{\text{Isoöctene}}{C_8H_{16}} + H_2 \longrightarrow \underset{\text{Isoöctane}}{C_8H_{18}}$$

c. Reduction of a carboxyl group to an alcohol



$$\underset{\text{Stearic Acid}}{C_{17}H_{35}COOH} + 2H_2 \longrightarrow C_{17}H_{35}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH + H_2O$$

Stearyl Alcohol

d. Hydrogenolysis

$$\text{Coal Tar} \xrightarrow[\text{Catalyst}]{H_2} \text{Motor or Diesel fuels}$$

The annual production of hydrogenated materials makes up a considerable proportion of all organic chemicals. The annual world production of hydrogenated fats is estimated to be in excess of half a million tons. These fats are used for the preparation of solid lard, butter substitutes, shortening compounds, soaps from liquid fats, for the manufacture of creams and coatings for confections, for leather dressings, for candle making, paint making, and for pharmaceutical ointments. A recent development of importance to the soap industry

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[52] See Groggins, P. H., "Unit Processes in Organic Synthesis." McGraw-Hill Book Co., Inc., 2nd ed. 1938. See pp. 413-18 for illustrations of various types of oxidation reactors.

is the hydrogenation of long chain fatty acids to form long-chain aliphatic alcohols.[53] The commercial preparation of methanol by the reaction of hydrogen with carbon monoxide or carbon dioxide amounts to about 30,000,000 gallons annually in the United States alone.[54] The hydrogenation of petroleum products is important to the petroleum industry for the preparation of gasoline and specialty products, as well as for improving such materials as kerosene, Diesel fuel, and lubricating oils.[55] In addition to the hydrogenation of other petroleum products some 90,000,000 gallons of technical isooctane were produced in 1938 in this country by hydrogenation of polymers of butylene and isobutylene. The hydrogenation of coals and coal tar is an important industry in Germany and England.[56]

Conditions for Hydrogenation. Hydrogenation reactions are usually carried out at temperatures varying from 150 to 250° C., though both lower and higher temperatures are sometimes used. For most cases, two opposing tendencies must be balanced in choosing the optimum reaction temperature. Increasing the temperature speeds up the reaction but also tends to affect the equilibrium adversely since the reactions are exothermic.[57] Fortunately, the development of effective catalysts has made it possible to use lower temperatures where equilibrium conditions are favorable and still maintain satisfactory reaction rates. Since most hydrogenation reactions result in a decrease in volume as the reaction proceeds, the degree of completion is favored by increasing the pressure. Hence, the use of pressure is common. The range of pressures used for hydrogenation of organic compounds varies from a few to over 200 atmospheres. Catalysts are essential in hydrogenation reactions, and a wide variety of them are available.

Equipment. Although high pressures are already used, the trend in commercial hydrogenations seems to be toward still higher pressures. The design of such equipment, however, is somewhat complicated, and it is necessary to use alloy steels. Equipment is available for both batch and continuous operations. Batch operations can be carried out in autoclaves provided with agitation and using a catalyst suspended in the material being hydrogenated.

Figure 5 shows one type of hydrogenator used in the hydrogenation of vegetable oils. These hydrogenators are operated at pressures varying from 20 to 75 pounds per square inch and temperatures varying from 325 to 450° F. In this reactor the catalyst is suspended in the oil which is sprayed into the top of the reactor. Hydrogen is bubbled into the bottom of the reactor to provide a countercurrent flow of the reactants. Internal heating coils provide for temperature control. The catalyst is kept in suspension by the action of the oil circulating pump, by the agitation produced by the hydrogen gas, and by the mechanical agitator mounted on the side of the reactor.

Figure 6 is a picture showing a hydrogenator similar to the one illustrated in Fig. 5, except that this unit has external heat exchangers instead of the internal heating coils, and no mechanical agitator is provided.

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[53] See Chapter 42.

[54] See Chapter 30.

[55] See Chapter 14.

[56] See Chem. and Met. Eng., *42*, 658-60 (1935), or Intern. Conf. Bituminous Coal, II, 49 (1931).

[57] See p. 97.

In continuous processes the catalyst is maintained stationary in forged steel reactors and the material being hydrogenated is passed through it continuously. Because of the thick reaction vessel walls which make heat transfer somewhat difficult, it is usually better to add all of the heat needed to the material before it gets to the reaction vessel. Since hydrogenation reactions are usually exothermic, it is sometimes necessary to remove heat once the reaction is started.

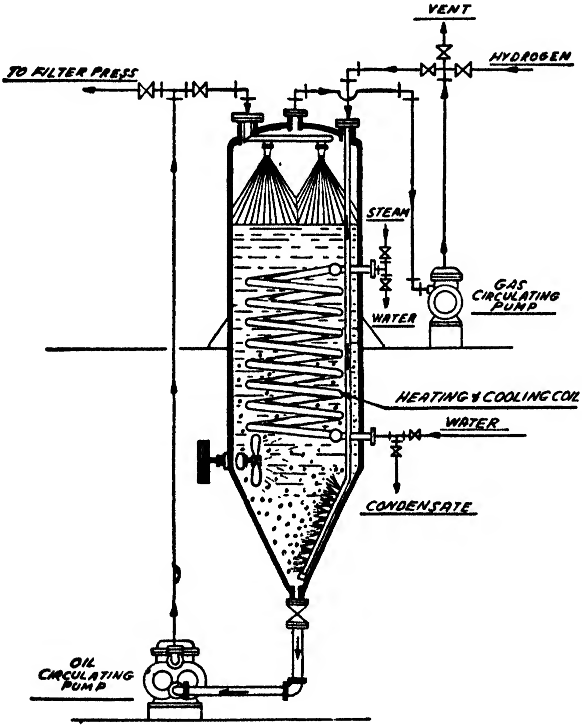
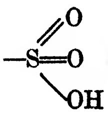


FIG. 5. Hydrogenator with Inside Heating and Cooling Coil, Oil and Catalyst Circulating Pump, Gas Circulating Pump, and Propeller-type Mechanical Agitator. (Courtesy Wuster and Sanger, Inc.)

This can be accomplished by heat exchange within the reactor, or by cooling part of the material outside the reactor and returning it to maintain the desired temperature.[58]

Sulfonation—Sulfonation is the process by which the  $-\mathrm{S}(=\mathrm{O})(=\mathrm{O})\mathrm{OH}$ group is united with a carbon or nitrogen of an organic compound.

In sulfonation with sulfuric acid, water is formed as one of the products of the reaction. One molecule of water is formed for each sulfonic acid group introduced into the compound being sulfonated.

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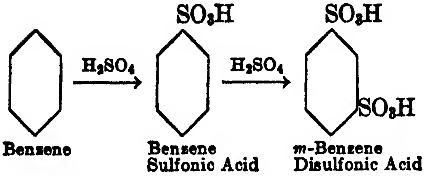
[58] For illustrations of high pressure equipment see Chapter 4.

Examples:



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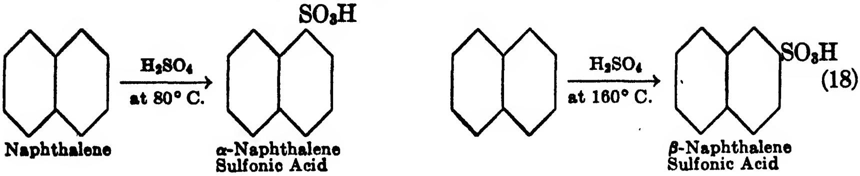

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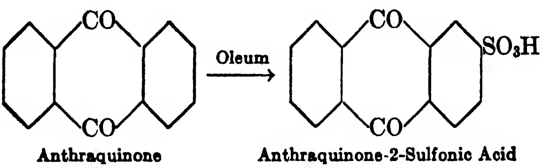

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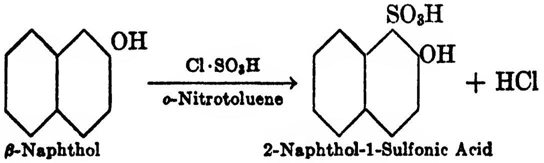

Sulfonic acids prepared by sulfonation reactions are used principally for the preparation of dyestuffs,[59] though some of them are used directly and as intermediates for other chemicals. Certain sulfonated oils, such as sulfonated castor oil, olive oil, and other vegetable oils [60] have long been used in the glue, paper, leather, and textile industries while others find special uses as wetting agents, detergents, and constituents of soaps.

Conditions for Sulfonation. Sulfonation reactions are carried out under a wide variety of conditions. Except for a few types of aliphatic compounds such as vegetable oils and unsaturated compounds, sulfonation reactions are limited to aromatic compounds. The following are important factors in sulfonation: strength of sulfonating agent, proportion of sulfonating agent to compound sulfonated, temperature of reaction, time of reaction, agitation, and the presence of catalysts. Concentrated sulfuric acid is the most common sulfonating agent, but the use of oleum or other agents, such as $Cl \cdot SO_3H$, SO_3, Na_2SO_3, is sometimes advantageous. The reactivity of H_2SO_4 as a sulfonating agent depends upon the SO_3 concentration, since it is known that sulfonation stops at a definite SO_3 concentration which is different for each compound undergoing treatment. Since water is formed in the reaction, it is necessary to add sufficient acid to prevent the SO_3 concentration from falling to this minimum value before the desired reaction is completed. In order to avoid a large excess of sulfonating agent the use of oleum

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[59] See Chapter 28.
[60] See Chapter 42.

to take up the water formed has been employed. Another method of accomplishing the same result is to carry out the reaction at a low temperature and distill off the water formed.

In sulfonation reactions, an increase in temperature not only accelerates the rate and degree of reaction, but also influences orientation. Most sulfonations are carried out at a temperature below 250° C. It is especially important to stop the reaction as soon as the desired conversion is reached in order to avoid polysulfonation, rearrangements, or migration where these are possible. Liquid-phase catalytic processes are the rule—the common catalysts being salts of vanadium, mercury, and alkali metals. Experience has shown that agitation is one of the principal requisites of good sulfonation practice. This is necessary to secure contact between the reactants as well as to prevent local overheating with its consequent ill effects.

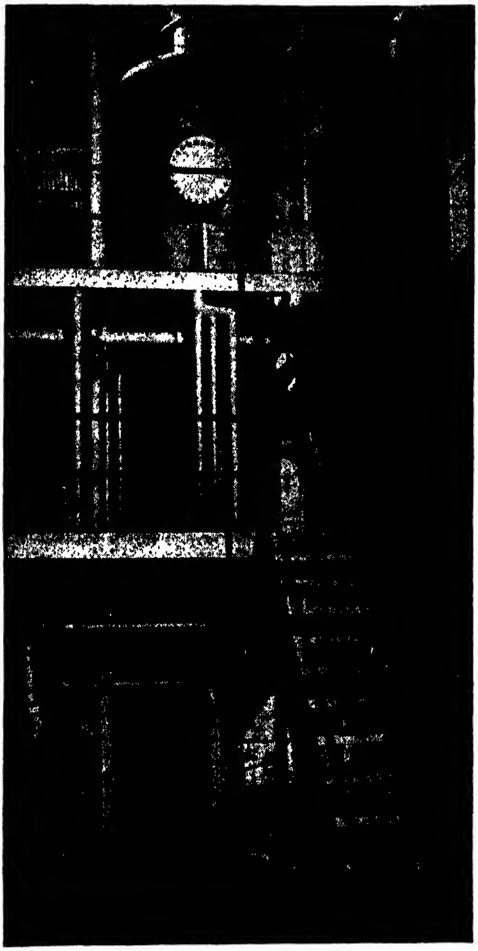


FIG. 6. Hydrogenator for Vegetable Oils. (Courtesy Wuster and Sanger, Inc.)

Equipment. In the construction of sulfonators, cast iron apparatus is suitable with concentrated acid of 88 to 98% strength, but steel equipment is desirable where oleum or a solution containing free SO_3 is utilized. The apparatus must provide for agitation and for heat transfer. Neither of these factors presents great difficulty and there are a number of commercial vessels designed for this unit process.

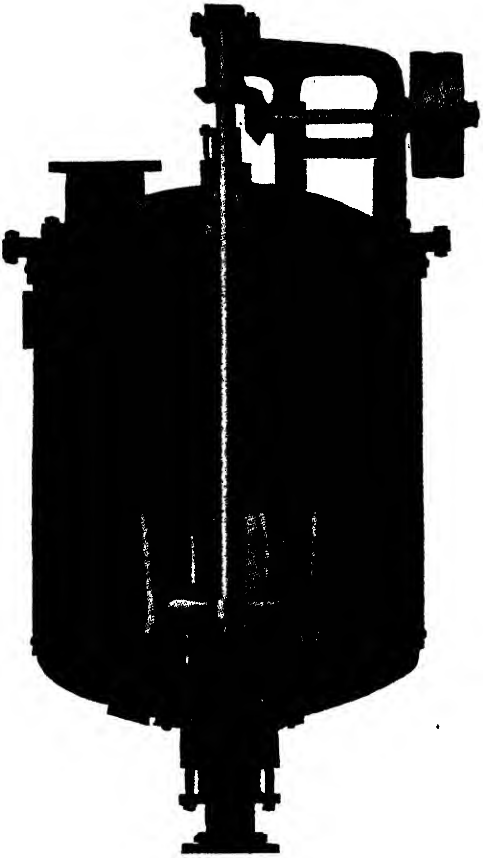


FIG. 7. Standard Cast Iron Sulfonator. (Courtesy Bethlehem Foundry & Machine Co.)

Figure 7 shows one type of standard sulfonator which is available in capacities from 50 to 2200 gallons. This sulfonator has a cast iron body and a full jacket of welded steel plate. The vaned draft-tube and marine type propeller provide very thorough agitation and mixing, but other types of agitators, such as horseshoe, beaters or scrapers may be substituted when desirable.

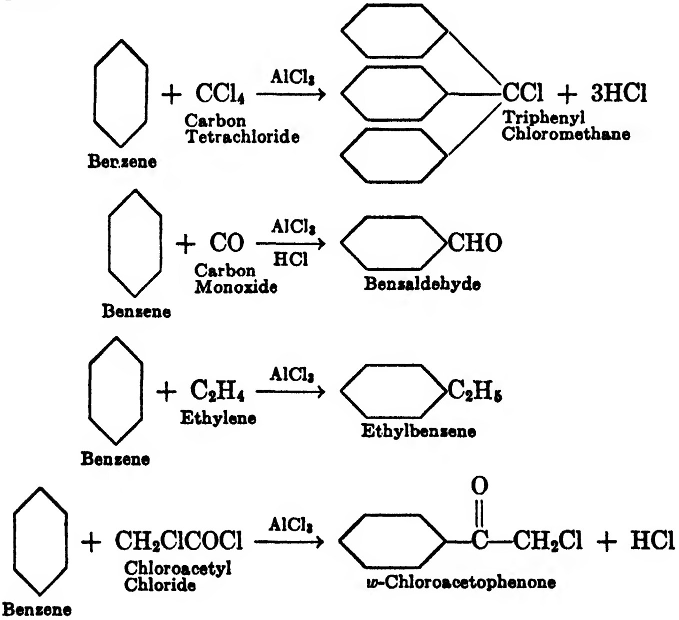
In cases where continuous heating or cooling is required, or where temperatures higher than those obtainable with low pressure steam are necessary, thermocoil sulfonators may be used. The chief characteristic of this type of sulfonator is a series of tubes cast into and integral with the walls of the vessel. The steel tubing and cast iron wall form a homogeneous mass insuring high efficiencies in heat transfer. The steel tubes are designed for high pressures so that high pressure steam or some other high temperature heating medium can be used. Since a number of inlets must be provided for the heating medium, the surface temperature of the vessel can be kept practically uniform and hence hot spots are eliminated.

The Friedel-Crafts Reaction—The term condensation is generally considered to include reactions in which union is effected between two or more of the same or different molecules, with or without the elimination of water or some other inorganic compound. Hence, condensation, in the broad sense, takes in such a variety of type reactions that it is not very helpful to consider it as a unit process. However, one type of condensation, known as the Friedel-Crafts reaction, is important enough to demand inclusion as a separate unit process.

An exact definition of the Friedel-Crafts reaction is impossible because it embraces such a variety of unusual but useful reactions. In the broad sense, any reaction catalyzed by a metallic halide may be considered as a Friedel-Crafts reaction. Taken in a narrow sense, however, this unit process is understood to involve the union of a comparatively active compound, such as ethyl chloride, ethylene, CO, CCl_4 or acetyl chloride, with a relatively stable hydrocarbon or substituted hydrocarbon, such as benzene or anisole, in the presence of the halides of metals such as Al, Fe, B, Sn, or Ti. Aluminum chloride is the usual condensation agent, and hydrochloric acid is usually eliminated in the reaction.

There are *two principal types* of Friedel-Crafts reactions: (1) the strictly catalytic type in which the aluminum chloride, or other halide, is always present in small amounts to act as a catalyst, and can be recovered and re-used; and (2) the type in which the aluminum chloride must be present in greater than catalytic amounts—at least one mole per mole of product.

Examples:



Uses of the Reaction. A wide variety of synthetic organic chemicals, such as hydrocarbons, aldehydes, acids, ketones, halogen compounds and other derivatives, can be prepared by Friedel-Crafts reactions. Acetophenone, propiophenone, benzophenone, benzaldehyde, benzoylbenzoic acid, ethyl benzene, phenyl ethyl alcohol, and tricresyl phosphate are a few of the compounds prepared on an industrial scale by this reaction. These materials are used as intermediates in dyes and perfumes, in the preparation of synthetic resins,[61] and as plasticizers for rubber and plastics.[62]

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[61] See Chapter 31.
[62] See Chapters 31 and 39.

Conditions for the Process. A number of chemical and physical factors have an important effect on the course and extent of the Friedel-Crafts reaction. The major ones are temperature, concentration of organic reactants, molal ratio of metal halide to organic reactants, purity of reacting chemicals, and size of aluminum chloride particles. The quantity and purity of aluminum chloride must be carefully regulated to obtain the maximum yield of the desired products. Many reactions are unfavorably influenced by impurities in the aluminum chloride, such as $FeCl_3$, $TiCl_4$, $MgCl_2$, excess HCl, etc. Impurities in the reacting chemicals may remove $AlCl_3$ as a double compound, making it no longer available to act as catalyst. The state of aggregation of the $AlCl_3$ has considerable influence on the process. It has been found that a fairly coarse type of $AlCl_3$, in the form of granules or small lumps, should be used with efficient agitation. The removal of the hydrochloric acid liberated by the reaction is desirable in most Friedel-Crafts syntheses. This is usually accomplished by drawing a slow stream of warm dry air over the charge. Control of the temperature at the optimum for a particular reaction is essential if good yields are expected. Moderate elevations in temperature not only affect orientation but also bring about secondary condensations. With excessive heating, almost all Friedel-Crafts reaction masses can be largely converted into oily masses of complex or uncertain composition. Friedel-Crafts syntheses are usually carried out in a liquid medium. An excess of one of the reacting materials may be used as the solvent, or a non-reactive solvent such as carbon disulfide, petroleum ether, acetylene tetrachloride, or nitrobenzene can be utilized.

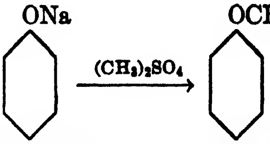
There is *no standard design of apparatus* for carrying out Friedel-Crafts reactions, but there are certain basic principles that can be applied to the design or selection of such equipment. The handling of aluminum chloride and certain other reagents must be done in a manner to avoid scrupulously the entrance of water into the system. Water not only causes hydrolysis of aluminum chloride, resulting in decreased yields, but also creates a corrosion problem due to the hydrochloric acid released by the hydrolysis. Due to the absence of moisture, most Friedel-Crafts reactions can be carried out in iron reactors. Certain compounds are adversely influenced by the presence of metallic iron at the reaction temperature, and such reactions are best carried out in enamel-lined or lead-lined reaction vessels. Some of the recently developed reactors have been made of the newer alloys which are resistant to the corrosive action of hydrochloric acid and acid chlorides.

Figure 8 shows one type of reactor for carrying out Friedel-Crafts reactions. It is fitted with a special plow-type stirrer which gives positive agitation and breaks the surface of the mass, permitting removal of the HCl liberated by the reaction, and also scrapes the material off the heat transfer surface, thereby permitting a high rate of heat transfer. The coils embedded in the walls are also a distinctive feature of this reactor. The design permits operation of the reactor under pressure or vacuum, and the HCl liberated by the reaction can be removed readily or retained in the reactor if desirable. A conveniently located door allows the material to be removed readily from the side of the reactor.

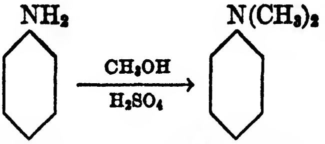
Alkylation[68]—Alkylation can be defined as the unit process whereby an alkyl or an aralkyl radical is introduced by addition or substitution into an organic compound. This process is used principally in one of the following five general types of reactions: (1) addition to a tertiary nitrogen; (2) addition to a metal to form alkyl-metallic compounds; (3) substitution for H in an —OH group of an alcohol or phenol; (4) substitution for hydrogen attached to nitrogen; and (5) substitution for hydrogen in carbon compounds. The following are some of the important reagents used: $(CH_3)_2SO_4$, $(C_2H_5)_2SO_4$, CH_3OH, C_2H_5OH, CH_3Cl, alkyl iodides, olefins and $C_6H_5CH_2Cl$.

Examples:

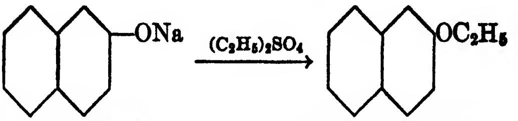
$$\underset{\text{Lead Sodium Alloy}}{4PbNa} + \underset{\text{Ethyl Chloride}}{4C_2H_5Cl} \longrightarrow \underset{\text{Tetraethyl Lead}}{Pb(C_2H_5)_4} + \underset{\text{Lead}}{3Pb} + \underset{\text{Sodium Chloride}}{4NaCl}$$



Sodium Phenolate **Anisole**



Aniline **Dimethyl Aniline**



Sodium β-Naphtholate **Naphthyl Ethyl Ether**

$$\underset{\text{Isobutylene}}{i\text{-}C_4H_8} + \underset{\text{Isobutane}}{i\text{-}C_4H_{10}} \xrightarrow{H_2SO_4} \underset{\text{Isoöctane}}{C_8H_{18}}$$

The products obtained by alkylation are used in making a great variety of materials, such as medicinal preparations, dyes, explosives, intermediates, plastics, solvents, rubber accelerators, perfumes, photographic chemicals, gasoline, etc.

Conditions for Alkylation. Because of the variety of materials prepared by alkylation reactions in addition to the diversity of alkylating agents which may be used, it is difficult to list the general conditions under which alkylation reactions are carried out. The concentration of alkylating agent may be high, particularly when alcohols are used as the alkylating agent. But sometimes it is advisable to dilute the alkylating agent in order to control the reaction better. Most alkylations are carried out in the liquid phase at temperatures below 200° C., but some are performed in the vapor phase at much higher temperatures—around 400° C. Pressure is necessary in numerous instances in order to keep the reac-

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[68] For a discussion of Alkylation as applied to petroleum products see page 139, and Chapter 14.

tions in the liquid phase. Catalysts are important in alkylation reactions, sulfuric acid being the most common catalyst. The proportions of reacting materials determine the type of products obtained. In some cases it is desirable to use an excess of alkylating agent to obtain better yields, but in others, especially where there is more than one place in the molecule where alkylation can take place, it is necessary to use only a limited amount of the agent.

Equipment. Alkylation reactions are usually carried out in autoclaves or jacketed kettles provided with agitation. The autoclaves are generally constructed of steel, with or without an anti-corrosion liner of lead, tinned iron, tinned copper, or enamel coated iron. The autoclaves can be heated directly or by the use of a heating medium circulated through a jacket or coils within the autoclave. By the use of alkylating agents with low vapor pressures, it is sometimes possible to carry out the reactions in agitated jacketed kettles of standard design.

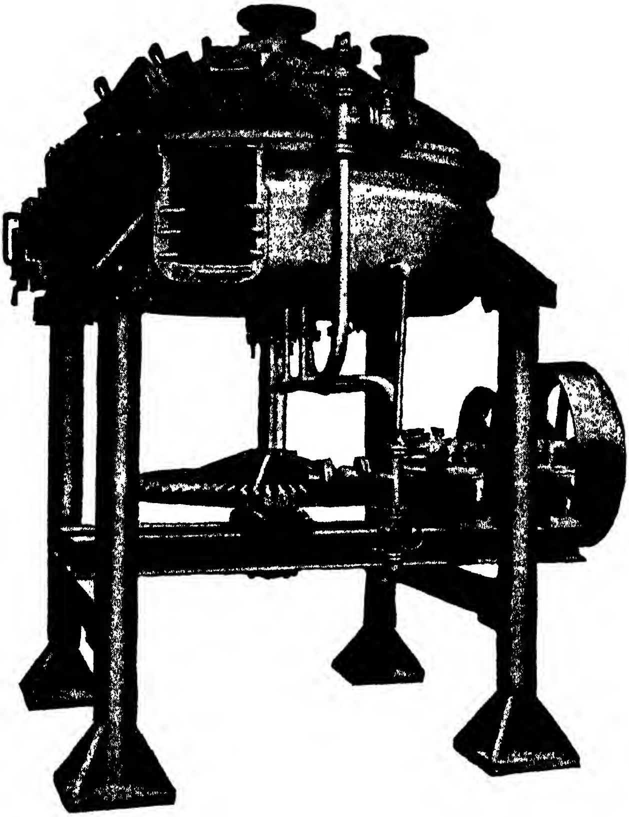

FIG. 8. Reactor for Friedel-Crafts Reactions. (Courtesy Bethlehem Foundry and Machine Co.)

Figure 9 shows a typical autoclave used for low pressure synthesis. This autoclave is jacketed and is provided with a motor-driven turbine type agitator.

For illustrations of high pressure autoclaves see pp. 116 and 117.

Polymerization[64]—"Polymerization can be defined as the chemical combination of a number of similar units to form a single molecule, wherein polymerization phenomena as well as condensation reactions occur."[65]

The unit process of polymerization has become increasingly important in the last three decades. During that period several thousand synthetic resins have been patented and quite a number are being produced on a commercial scale. The synthetic resins[66] are being used more and more as substitutes for glass, ceramic ware, wood, bone, metals and alloys, in addition to filling many needs for structural materials which could not be supplied by any other substances available at any price. The weight of synthetic resins produced annually in the United States amounts to over 200,000,000 pounds.[67]

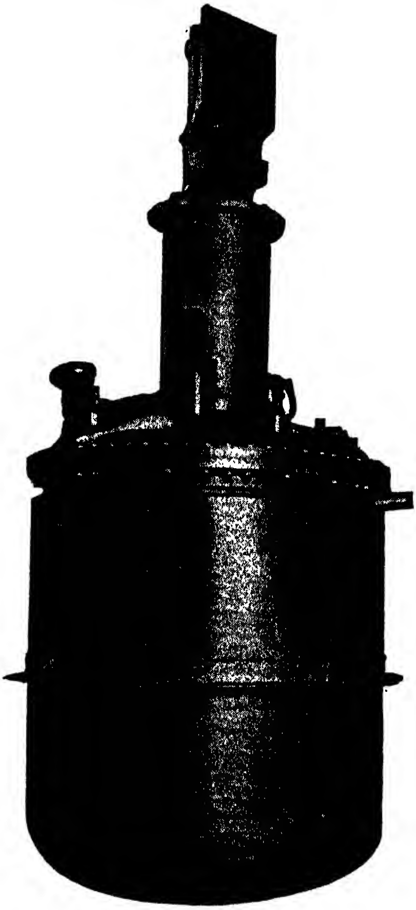

FIG. 9. Autoclave for Low Pressure Synthesis. (Courtesy Blaw-Knox Co.)

Despite an enormous amount of experimental work, much of the chemistry of polymerization is still unknown. In the preparation of synthetic resins, condensation as well as polymerization reactions may occur, especially in the early stages of the reaction. The final products obtained are exceedingly complex, high molecular weight materials which make structural determinations almost impossible. Enough is known about the reaction conditions, however, to permit many useful materials to be made.

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[64] See Chapter 14 and p. 139 for a discussion of polymerization as applied to petroleum products.

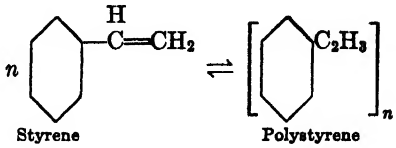
[65] Carothers, W. H., J. Amer. Chem. Soc., *51,* 2548 (1929).

[66] See Chapter 31.

[67] Figures are for 1939. See Chapter 31 for a description of the most important synthetic resins.

Examples of polymerization reactions:

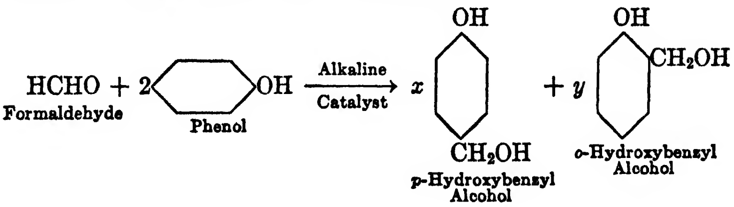
Polymerization[68, 69]



$x\ HCHO \longrightarrow (CH_2O)x$

Formaldehyde Polyoxymethylene

Combined Polymerization and Condensation[68, 69]



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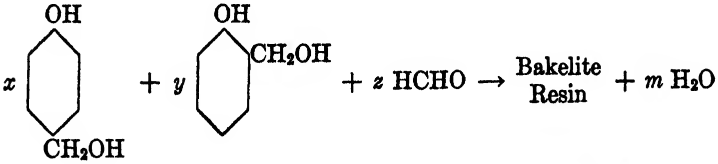

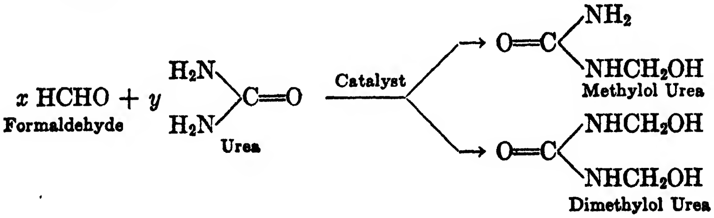

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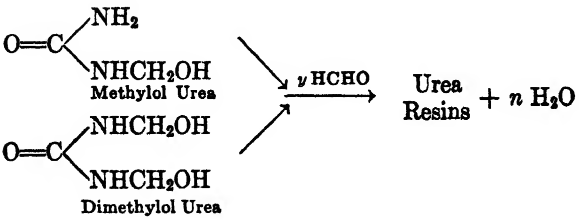

The *conditions used in the preparation of synthetic resins* depend not only upon the reacting materials but also upon the type of products desired. By making suitable changes in the reaction conditions it is possible to obtain a great variety of products from essentially the same basic raw materials. The products obtained depend upon a number of factors such as heat, light, pressure, catalysts,

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[68] The symbols x, y, z, m and n are put in to indicate that the exact proportions are indeterminate.

[69] See Chapter 31.

time of reaction, and concentration, as well as the chemical character of the reactants themselves. The presence of certain unsaturated linkages in one or more of the reactants seems to be one of the important characteristics of the raw materials. Polymerization reactions are sensitive to heat, and control of the temperature is essential in the building of large molecular-weight products. Some of the common methods used to control the temperature are as follows: use of moderate-sized reaction chambers with good mixing, dilution with solvents, carrying out the reaction under vacuum, or maintaining the reaction mass at the boiling point of one of the reactants. Catalysts are important in polymerization reactions, many of the commonly used acids, salts, alkalies, peroxides, and oxides being employed. Pressure is another important factor in effecting polymerization reactions, especially where secondary condensations or rearrangements are involved. The removal of volatile products of the reaction under reduced pressure often helps govern the reactions as well as assists in controlling the reaction temperature. On the other hand, high pressures are sometimes desirable especially where volatile reacting materials are used and where high temperatures are needed. Solubility also plays an important part in polymerization reactions. It is necessary that all of the constituents obtained be mutually soluble at all temperatures and under all conditions so that there will be no tendency for separation of one of the constituents with its consequent ill effects on the finished article.

The equipment used for resin manufacture usually consists of some type of autoclave fitted with the necessary equipment for controlling the reaction. Several illustrations of typical autoclaves may be found in the discussion of the other unit processes in this chapter.

Figure 10 shows a set-up used in making resins for varnishes. The autoclave is made of chrome steel and is electrically heated. The turbine type agitator provides good mixing so that the reaction mass is kept almost homogeneous.

Thermal Decomposition (Pyrolysis)—Thermal decomposition is a unit process of vast importance to our industrial civilization. The decomposition of wood furnishes charcoal, acetic acid, methanol, etc. The pyrolysis of coal furnishes not only gas for industrial and domestic heating purposes, and coke, an essential material to the metallurgical industries, but also supplies the raw materials for the important aromatic organic chemicals industry. The thermal decomposition of petroleum is also of great importance in converting certain petroleum fractions into more valuable products. Since the decomposition of each of these raw materials provides the basis for a large industry, the decomposition of each material will be discussed separately.

Thermal Decomposition of Wood.[70] Wood consists principally of three materials: cellulose, 40 to 63%; lignin, 24 to 37%; and hemicelluloses, 6 to 20%.[71] Most woods also contain from 0.2 to 1.0% ash, 0.1 to 0.3% nitrogen, and varying amounts of gums, tannins, volatile oils, fats, waxes, resins, and coloring matter.

The exact chemical nature of the principal constituents of wood is unknown, though a great deal is known concerning their properties. Cellulose is known to have the empirical formula $(C_6H_{10}O_5)x$ but the exact

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[70] See also Chapter 17.

[71] Schorger, A. W., "The Chemistry of Cellulose and Wood," McGraw-Hill Book Co., Inc. 1926. Especially pp. 24-68.

value of x is still uncertain. Brauns and Hibbert[72] have suggested the formula $C_{42}H_{32}O_6(OH)_5(OCH_3)_5$ as the minimum formula for lignin which will satisfy all of the known facts concerning that substance. This formula, however, has not been definitely proved to be the true one. The hemicelluloses defy simple classification but they may be broadly defined as polysaccharides (mostly pentosans and hexosans) soluble in dilute alkali and convertible into sugars by acid hydrolysis at atmospheric pressure. Hence, they also are compounds composed of carbon, hydrogen, and oxygen, similar to cellulose.

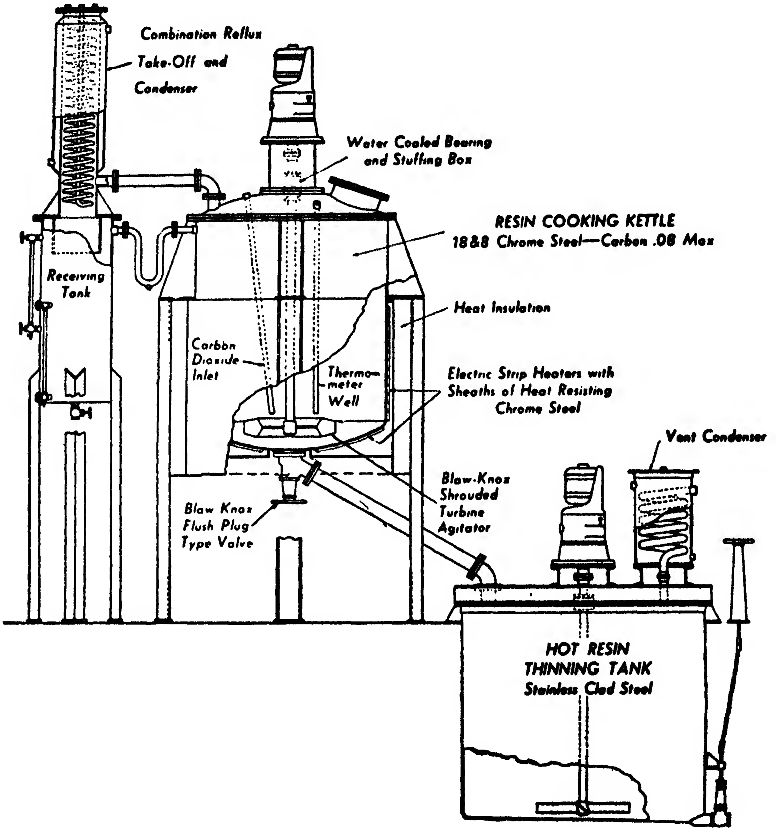

FIG. 10. Apparatus Used for Making Resins for Varnishes. (Courtesy Blaw-Knox Co.)

The destructive distillation of wood for the preparation of charcoal with the recovery of organic chemicals as by-products has been a well established industry in the United States for a number of years. Synthetic methods for producing organic chemicals, normally recovered as by-products of this industry, seriously threatened its existence. Due to the continued demand for charcoal and to technological improvements, however, it is now in a more secure financial position.[73]

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[72] Brauns, F., and Hibbert, H., J. Amer. Chem. Soc., *55*, 4720 (1933).
[73] See also Chapter 17.

The thermal decomposition of wood is chemically complex. The raw material is made up of several complex constituents which probably have different decomposition temperatures. Moreover, these constituents seem to decompose in a manner which is dependent upon the temperature. Ordinary wood is not uniform throughout, and the products formed upon heating depend upon the size of the wood pieces heated. In addition there is the possibility that a number of the original decomposition products undergo further changes before they are removed from the reaction zone, and, hence, the end products may not throw much light on the actual mechanism involved.

Sequence of Reactions. When heated in the absence of air, wood begins to evolve water and carbon dioxide at comparatively low temperatures. When the temperature reaches the neighborhood of 280° C. gas evolution proceeds rapidly and the reaction changes from an endothermic to an exothermic one. Noncondensable gases such as hydrogen, carbon monoxide, carbon dioxide, methane, and illuminants are evolved, besides many aliphatic chain compounds, such as acids, alcohols, esters, and ketones. A tar is also formed, particularly at high temperatures, which contains various aromatic compounds, such as phenols. The higher the temperature employed the greater the quantities of noncondensable gases found, and the smaller the yields of condensable products. The residual charcoal contains a higher percentage of carbon as the temperature of decomposition is raised.

There is some doubt as to the source of the various important chemicals obtained from the destructive distillation of wood, though distillation of the major constituents separately gives some indication of the sources. Lignin is probably the source of methanol and higher phenols. Cellulose yields little methanol but considerable acetic acid, while cellulose tar yields principally phenol. Pentosans give acetic acid and considerable furfural, in addition to the usual gas and tar by-products. Allyl alcohol, ammonia compounds, amines, and pyridine are also usually found in the products in relatively small amounts.[74]

The destructive distillation of agricultural wastes yields materials similar to those obtained from wood.[75]

The *thermal decomposition of coal* is of great industrial significance since this process not only furnishes fuels but also the raw materials for aromatic chemicals. The decomposition of coal is carried out to obtain three principal types of products: namely, (1) gas for industrial and domestic heating, (2) coke, for heating purposes and for the metallurgical industries, and (3) aromatic chemicals. The annual consumption of coal is in the neighborhood of 450,000,000 tons,[76] while the known reserves in the United States alone amount to over three trillion tons,[77] so that the supply seems to be ample for many years to come.

It is believed that coal originated from the partial decomposition of vegetable matter through the action of moisture, heat, pressure, and bacteria over long periods of time. All vegetable matter has a chemical composition similar to that of wood, but the constituents are present in different proportions from those found

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[74] For a description of the actual distillation process, see Chapter 17.

[75] Jacobs, P. B., Ind. and Eng. Chem., *32*, 214 (1940).

[76] Furnas, C. C., "The Storehouse of Civilization," Bureau of Publications, Teachers College, Columbia University, New York. 1939. P. 209.

[77] Lilley, E. P., "Economic Geology," p. 255, Henry Holt and Co., New York, 1936.

in wood. One theory of coal formation is that decomposition of this vegetable matter to form coal occurred with the elimination of compounds containing carbon, oxygen, and hydrogen, such as CH_4, H_2O, CO, and CO_2, leaving a material remaining which had a higher percentage of carbon than the original vegetable matter. During the decomposition process the material lost its cellular structure and the cellulose, lignin, and hemicelluloses no longer retained their identity.

The destructive distillation of coal yields products similar to those obtained from wood, but in different proportions. The products obtained depend upon such factors as the following: type of coal; temperature, time, and pressure of decomposition; catalysts; type of coking oven used; etc. In general, higher yields of aromatic compounds and nitrogen compounds are obtained from the decomposition of coal than from wood. Because of the importance of the coking industry, the thermal decomposition of coal is treated in detail in a separate chapter.[78]

The *thermal decomposition of petroleum* will be discussed under the heading Unit Processes of the Petroleum Industry, which is presented in the next section.

Unit Processes of the Petroleum Industry [79, 80]—The petroleum industry makes use of a number of unit processes. For convenience these processes are discussed together, but it should be noted also that in actual practice they do occur simultaneously. These processes in the past have been thermal reactions almost exclusively but within the last five years the trend has been strongly toward catalytic reactions.[81] The unit processes included in this section are as follows:

Cracking (thermal decomposition, pyrolysis)
Hydrogenation
Dehydrogenation
Alkylation
Polymerization
Isomerization
Aromatization (cyclization)

Definition of Terms. Before discussing the factors involved in the various unit processes used in petroleum refining, a brief discussion of the scope and meaning of each process will be given. The terms thermal decomposition and pyrolysis refer to the breaking up of large molecules into smaller ones by the action of heat. In referring to petroleum products this is usually called "cracking." Originally only high boiling stocks, such as kerosene, gas oils, and residues, were used as charging stocks for cracking and it was thought that the action was solely one of decomposition. Now almost any petroleum product, including gases, may be used as the charging stock and it is known that polymerization and condensation reactions occur simultaneously with decomposition at the conditions usually employed for cracking.

From cracking processes a number of low molecular weight saturated and unsaturated hydrocarbons are obtained in addition to those required for gasoline.

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[78] See Chapter 15.

[79] Clarke, M. E., Chem. and Met., *46*, 470-73 (1939).

[80] See Chapter 14.

[81] Berkman, S., Morrell, J. C., and Egloff, G., "Catalysis," Reinhold Publishing Company, 1940 (especially pp. 1001 to 1087).

These hydrocarbons serve as the raw materials for most of the other unit processes. By polymerization, unsaturated hydrocarbons, particularly propylene and butylene, are united to form longer chain unsaturated compounds which can be converted into saturated hydrocarbons in the gasoline range by hydrogenation. Unsaturated hydrocarbons, such as the butylene and propylene produced by cracking, can also be made from saturated aliphatic hydrocarbons by dehydrogenation. Alkylation accomplishes the purposes of both polymerization and hydrogenation by combining in one step a saturated iso-hydrocarbon with an unsaturated hydrocarbon to produce longer chain saturated hydrocarbons. Isomerization is used to convert straight chain saturated hydrocarbons into branched chain hydrocarbons which have higher anti-knock characteristics.

Aromatic hydrocarbons are usually more valuable than aliphatic or naphthenic hydrocarbons and several methods are available for synthesizing aromatics from these materials. The conversion of an aliphatic hydrocarbon into an aromatic hydrocarbon is called aromatization or aromatic cyclization. The conversion of an aliphatic hydrocarbon into a cycloparaffin is called cyclozation.

Cracking. The oldest and most important unit process of the petroleum industry is cracking, or pyrolysis. By cracking processes, the yield of gasoline from crude oil has been more than doubled. This has resulted in an estimated saving of more than 13,000,000,000 barrels of crude oil.[82]

The primary purpose of cracking is to increase the yield of high anti-knock gasoline from a crude oil. For that purpose a number of cracking processes have been developed. These processes can be classified under the following headings:

1. *Viscosity-breaking.* Conversion of viscous heavy crudes and residues into fuel oils of low viscosity by a short-time decomposition, usually conducted at low cracking temperatures (800 to 875° F.).
2. *Mixed-phase non-catalytic cracking.* A number of the important cracking processes fall in this classification. The mixed-phase processes are carried out at temperatures ranging from 820 to 1100° F. and at pressures varying from 50 to 1500 pounds per square inch. As usually practiced, the operation is carried out with moderate conversions per pass combined with recycling of a clean distillate stock. Recently, selective cracking in combination units has been finding favor. This process is based on employing the optimum conditions of time, temperature, and pressure for each fraction of the charging stock.
3. *Vapor-phase cracking.* The vapor phase processes are not as common as the mixed-phase process and are usually more expensive. The operating pressures are lower, usually less than 75 pounds per square inch, and the temperatures higher (1000 to 1200° F.) than for mixed-phase processes. Only comparatively light distillates can be processed and it is important to get a homogeneous phase. If any liquid is present, it is thrown to the tube walls and causes the formation of coke. The quantity of gas produced is greater, and the yield of gasoline lower than for mixed-phase processes. The gasoline produced, however, has a high anti-knock rating and can be sold at a premium price as a blending stock.

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[82] Egloff, G., Petroleum Engineer, *12,* 21 (1940).

4. *Reforming.* A cracking process for converting low octane number gasoline or naphthas into high octane number products. The process is carried out in mixed-phase or vapor phase with or without the presence of catalysts. Dehydrogenation, decomposition, and aromatization reactions take place in the process. The naphthenes and paraffins present in the feed stock are partially converted to olefins and aromatics, and some low molecular weight gaseous compounds are also produced. Reforming operations are carried out under fairly severe conditions. The temperatures range from 930° to 1040° F. and the pressures from 250 to 1000 pounds per square inch.
5. *Coking.* A cracking operation carried out under conditions such that coke instead of a liquid residue is obtained. This is accomplished by keeping the material at cracking temperatures long enough for complete decomposition of high molecular weight materials to take place.
6. *Catalytic cracking.* Catalytic cracking has become of commercial importance only within the last five years, but has already become an important adjunct to thermal processes. The temperature conditions used in catalytic cracking are very similar to those used in thermal cracking, but lower pressures are usually employed. The catalysts used in these processes do not appreciably affect the rate of reaction but do exert a directive influence on the reactions that take place. In these processes temperature control is of paramount importance. The cost and life of the catalyst and the cost of regeneration are items which must be considered in an installation of this type.

Two types of hydrogenation are practiced commercially on oil products; namely, simple and destructive hydrogenation. Simple hydrogenation consists merely of addition of hydrogen to carbon-carbon double bonds and is exemplified by the hydrogenation of isooctene to isooctane. Most of the commercial installations for hydrogenation, with the exception of equipment for isooctane production, are examples of destructive hydrogenation. This type of hydrogenation involves the breaking of carbon to carbon bonds and the addition of hydrogen to the products formed. Hence, it may be considered as a combination of simple hydrogenation with polymerization, cracking, dehydrogenation, cyclization, etc. A wide variety of charging stocks can be employed for destructive hydrogenation and the materials obtained vary from aviation gasoline to lubricating oils. The temperatures employed in destructive hydrogenations are so high (750 to 1050° F.) that cracking reactions take place simultaneously. Because of these high temperatures it is necessary to employ high hydrogen pressures—usually around 200 atmospheres. Though not essential to petroleum hydrogenation reactions, catalysts are advantageous and are generally used.

Dehydrogenation[83] is one of the more recent developments in the application of unit processes to petroleum processing. The general use of the term is so broad that it is almost useless to refinery technologists. Hence, its use is generally restricted to the dehydrogenation of materials boiling within the gasoline range or lower. Both non-destructive and destructive hydrogenation may be accom-

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[83] Grosse, A. V., and Ipatieff, V. N., Ind. and Eng. Chem., *32*, 268-72 (1940).

plished. The former term refers to the removal of hydrogen from hydrocarbons without cracking, while the latter term indicates that rupture of the molecule occurs in addition to the removal of hydrogen.

Non-destructive dehydrogenation is catalytic, but destructive dehydrogenation can be carried out either with or without catalysts. In the dehydrogenation of a paraffin hydrocarbon, the formation of hydrogen is favored by increasing the temperature and by using a low pressure. Accordingly, temperatures above 950° F. and atmospheric pressure is used for the process. The principal use of the olefins formed is as a charging stock for alkylation.

Alkylation. The broad use of this term has already been discussed (p. 129). In the petroleum industry its use is restricted to alkylation processes employing low molecular weight materials for the production of high octane number gasoline. Both catalytic and thermal processes are in use. The catalytic process is carried out at low temperatures, 30° to 100° F., and atmospheric pressure.[84] In this process isobutane is combined with isobutylene to give almost pure isooctane. The thermal alkylation process represents the other extreme, operating at 920 to 960° F. at about 4500 pounds per square inch. In this process ethylene is combined with isobutane to produce neohexane.[85]

Figure 11 shows one type of reactor used for the low temperature alkylation of hydrocarbons from petroleum using sulfuric acid as the catalyst. In this reaction contact time, temperature, and agitation are important variables which are dependent upon the type of equipment used. In the contactor illustrated, thorough agitation is provided by a pump which circulates the oil-acid mixture through a series of baffles and over the tubes of the heat exchanger. Close temperature control is provided by the heat exchanger, which forms an integral part of the contactor. Time of contact can be adjusted by regulating the amount of material recycled.

Polymerization [86] is used to a greater extent than any of the other unit processes in oil refining except cracking. Both thermal and catalytic processes are employed and low molecular weight hydrocarbons are used as the charging stock. The thermal process operates at high pressures and high temperatures but utilizes part of the saturated hydrocarbons as well as the unsaturates in the charge. Thermal polymerization processes are carried out at temperatures around 1000° F. under pressures varying from 600 to 2500 pounds per square inch. Catalytic polymerizations also are carried out under high pressures, 150 to 1500 pounds per square inch, but the temperatures are much lower than in thermal polymerizations, around 175° to 400° F. In these processes only unsaturated hydrocarbons are polymerized.

Isomerization and aromatization are just beginning to be used commercially and their economic positions have not been fully established at the present time.

Isomerization is used to produce isobutane and isopentane from their normal isomers. The process is catalytic and is carried out at 200° F. under a pressure of 200 pounds per square inch.

Aromatization (or aromatic cyclization) plants are in operation but the

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[84] MacKenzie, K. G., Refiner, *18,* 494-503 (1940).

[85] Oberfell, G. G., and Frey, F. E., Refiner, *18,* 486-493, 503 (1940).

[86] Koehler, W. A., Chem. and Met., *45,* 412-15 (1938).

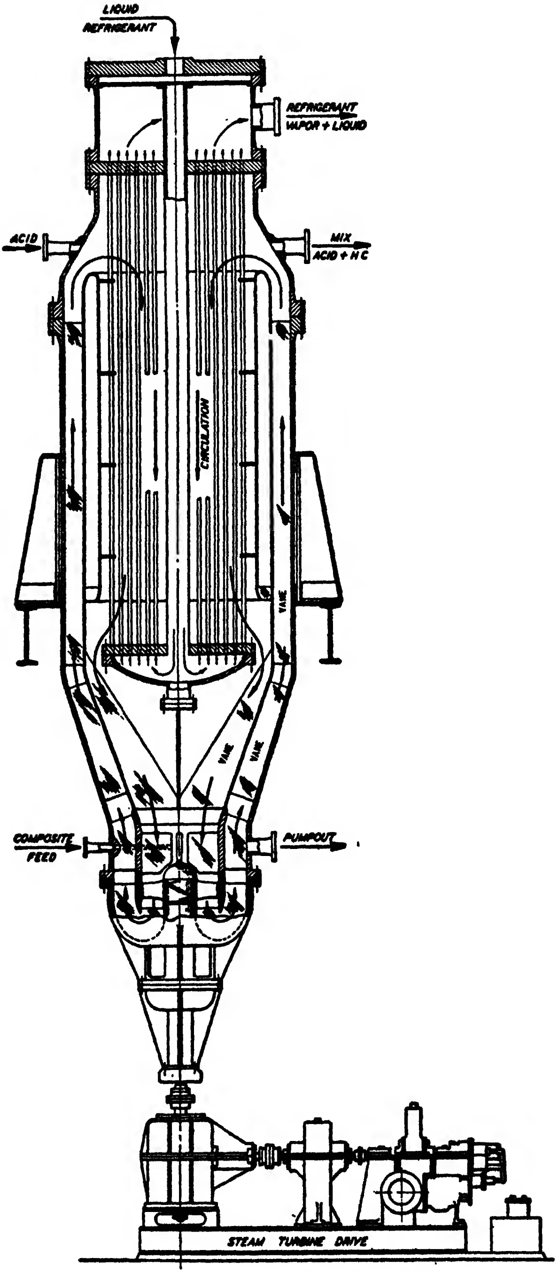

Fig. 11. Contactor for Sulfuric Acid Alkylation Process. (Courtesy Stratford Engineering Corp.)

details of the processes have not been divulged up to the present time. It is known, however, that low pressures (atmospheric to 40 pounds gauge) and very high temperatures (1100° F. and higher) favor this unit process. Toluene is being prepared from petroleum by this process.[87]

The *equipment used for the unit processes of oil refining* is practically all "tailor-made" for each installation. The reaction vessels or chambers are probably the most specialized pieces of apparatus employed. The high temperatures necessary in most cases are obtained by passing the material through tubes placed in gas or oil-fired furnaces. The equipment used for separation of the reaction products consists of standard types of unit operations equipment. (See Chapters 2 and 14 for illustrations.)

Miscellaneous Unit Processes—There are a number of miscellaneous unit processes such as neutralization, condensation, acylation, nitrosation, carboxylation, decarboxylation, molecular rearrangement, etc., which could be included in a discussion of this kind. Acylation and condensation reactions are included to a certain extent in the Friedel-Crafts reactions. Applications of the other unit processes have been so limited or the data available so insufficient that correlations on the basis of unit processes are impractical. However, it is recognized that some of these unit processes may become very important in the future.

READING LIST

Much information concerning the industrial applications of the unit processes is given in the other chapters in this book. Chapter 27 on Industrial Organic Chemicals and Dye Intermediates gives a summary of the methods of preparation and uses of a number of important organic chemicals. More specific information concerning the unit processes may be found in the following reading list.

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[87] Anon., Chem. and Met., *47*, 535-37 (1940).

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CHAPTER 4

HIGH PRESSURE PROCESSES

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One of the outstanding developments of the chemical industry during the past two decades has been use of high pressure processes. Not only have well-known products been made by new and more economical processes operating at high pressures, but new chemical syntheses have been made possible and commercially feasible. In some cases the development of high pressure processes has opened up completely new fields of chemical development. For instance, the large plant of the du Pont Company at Belle, West Virginia, is entirely based on pressure operations. Starting from coal, water, and air as raw materials, more than 100 different products are manufactured, which find wide application throughout all industry.

Products such as ammonia, methanol and urea had been made commercially for many years by other processes which have now been largely supplanted by the newer pressure processes. For example, prior to the direct synthesis process, ammonia was obtained largely as a by-product of the coking of coal and this placed a definite limit to the amount that could be produced.

Another source of ammonia was calcium cyanamide and the process for producing it in this way was developed on a large scale but, due to high power requirement and handling costs on large amounts of solid materials, it did not offer the promise of a truly cheap and abundant source of ammonia and has been almost entirely abandoned in favor of the direct synthesis.

The freeing of ammonia from its dependence on the processing of coal caused a veritable revolution in the whole economy of chemical industry. A cheap and unlimited supply of fixed nitrogen in a form readily converted to nitric acid has had an effect on the development of the chemical industry whose importance it would be difficult to exaggerate. Ammonia has become not only a cheap raw material for the chemical industry but also may hold the key to cheap fertilizers for agriculture. It is of the utmost importance to national defense as a raw material for nitric acid manufacture.

A similar story can be told with reference to methanol, which prior to its direct synthesis was available only as a by-product of hard wood distillation.[1] As a result of the introduction of the high pressure synthesis, the price dropped from $1.30 per gallon to about $.40 in a relatively short time and it is probable that it can be produced for less than $.20 per gallon (about $.16 is a fair average). A relatively cheap and unlimited source of it was a great stimulus to the

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[1] See Chapter 17.

development of the phenol-formaldehyde plastics which depend on methanol as a raw material.

Other high pressure developments at the Belle plant have led to entirely new products such as the methacrylate plastics and nylon, both of which are made from intermediates derived from high pressure synthesis.

A field of activity which is only some 20 years old undoubtedly has a long period of growth ahead of it, so it is to be expected that the future will see many new developments coming from high pressure operations.

High pressure operations and processes do not differ qualitatively from the operations and processes discussed in the previous two chapters but the use of high pressure presents special possibilities and problems which are worthy of special consideration.

For the present purpose, high pressure will be defined as pressures above 50 atm. (750 lbs. per sq. in.). Pressures as high as 1000 atm. are now used in chemical industry and higher ones could undoubtedly be employed, provided the temperature is not too high, if there were any good reason for their use. At the present time even 1000 atm. is rather uncommon and most high pressure processes operate under 500 atm. Very much higher pressures (of the order 3,000,000 lbs. per sq. in.) have been produced on a laboratory scale and pressures of the order of 500,000 lbs. per sq. in. are estimated to be produced in some gears and bearings. Pressures of the order of 50,000-75,000 lbs. per sq. in. are developed in heavy artillery. Many laboratories both in industry and in the universities are investigating properties and reactions under "super" pressures and one may confidently expect that in the not far distant future, pressures higher than those now in use will find application in industry.

The effect of high pressures on the physical properties of substances has been studied in laboratories for more than 100 years. The work of Amagat is typical of the older, classical work in this field. The study of chemical reactions under pressure practically began with the pioneer work of Ipatieff in Russia (about 1900) and Haber (1904) in Germany. The pioneer industrial developments were the Haber-Bosch process for ammonia synthesis (1910-13) and the Burton process for oil cracking (about 1913). Though the latter could not be classified as a high pressure process, yet it was the forerunner of present high pressure processes used in the petroleum industry.

REASONS FOR USE OF PRESSURE

There are only two primary reasons for the use of pressure in chemical processes, viz.:

(1) to shift equilibrium
(2) to maintain a liquid phase

Effect of Pressure on Equilibrium—Qualitatively, the effect of pressure on any chemical equilibrium is to shift it in the direction of a volume decrease according to the Le Chatelier-Braun principle. The quantitative effect is given by well-known thermodynamical principles first worked out in rigorous and general form by Willard Gibbs. For good first approximations it can be assumed that the effect of pressure on the equilibrium of liquid phase reactions is negligible and that for gas reactions, the equilibrium constant in terms of partial pressure, K_p, is independent of the pressure.[2]

For a rigorous treatment one must take account of the fact that the equilibrium constant as well as the equilibrium state varies with the pressure. For example, in the case of the ammonia equilibrium, the equilibrium constant at 450° C. increases 3.5 fold as the pressure increases from 1 to 1000 atmospheres.

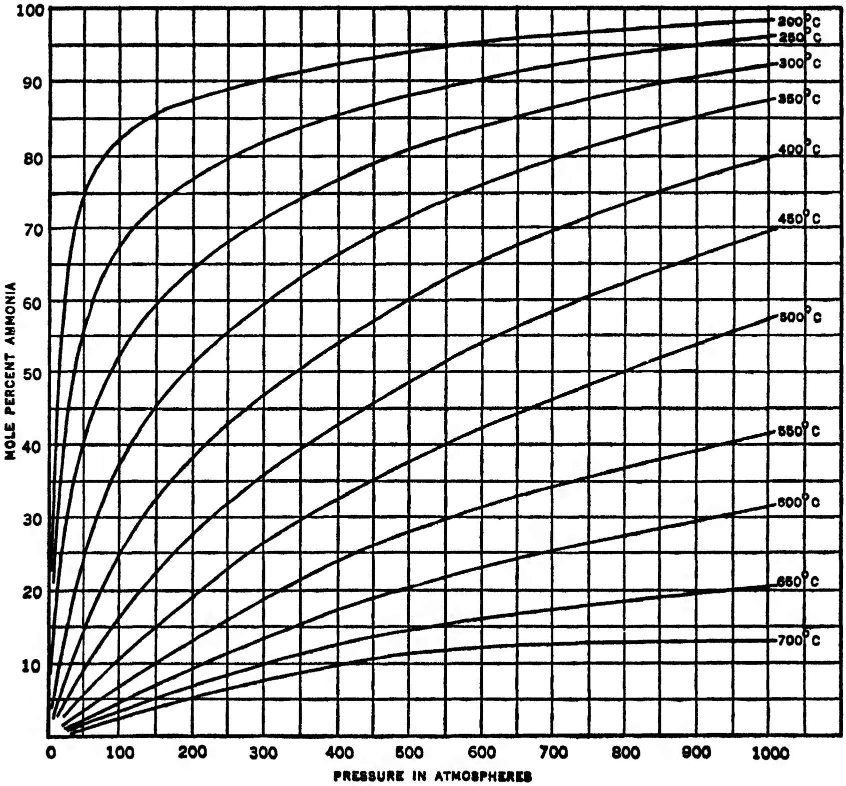

FIG. 1. Equilibrium Per Cent Ammonia in a 3 to 1 Hydrogen-Nitrogen Mixture.

In the case of the methanol equilibrium the effect may be even greater depending on the temperature.[3]

A typical example of the effect of pressure on chemical equilibrium is given by the data on the ammonia synthesis equilibrium shown in Figure 1. It is not at once evident from a study of this figure why high pressures are necessary in this process because if the reaction could be carried out at 200° C. good conversions would be obtained at low pressures. This brings out the fact that equilibrium must always be considered in conjunction with reaction rate.[4] No practicable catalyst has been discovered which will permit the carrying out of this reaction

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[2] See Chapter 3.

[3] For a more complete discussion of this subject see paper by Dodge, B. F., Trans Am. Inst. Chem. Engrs. ***34***, 529 (1938).

[4] See Chapter 3.

at less than 400° C. and in most cases the gases leave the catalyst at a temperature between 500 and 600° C. Thus it may be said that the reason for using pressure is to counteract the unfavorable effect of temperature on the equilibrium.

The degree of conversion continues to increase with the pressure but above about 900 atm. any gain from this increase is more than offset by the practical difficulties of working at higher pressures. In fact, some engineers with experience in this field believe that the point of diminishing returns is reached at about 350 atm. In laboratory experimentation ammonia has been synthesized at pressures as high as 5000 atm. It is of interest to note that at such a high pressure, almost complete conversion to ammonia can be achieved without the aid of any catalyst.

Maintaining a Liquid Phase—The second main reason for carrying out reactions under pressure is the very simple one that pressure is necessary to maintain a condensed phase. In such a case the reaction is carried out at the vapor-pressure of the system and naturally at a temperature below the critical. In this category we may place such processes as the production of phenol[5] by liquid-phase hydrolysis of chlorbenzene and the liquid-phase cracking[6] of petroleum oils. It is recognized that the pressure may have other concomitant effects such as shifting the equilibria but the primary reason for its use is to "keep the liquid in the pot."

The upper limit in such a case is the critical pressure of the system, the highest pressure at which a liquid phase is possible (this strictly applies only to a single component; for binary and multi-component systems, liquids are possible over limited composition ranges, at pressures considerably higher than the critical). Most organic liquids have critical pressures around 40-60 atm., whereas for water it is 218 atm.

Other Advantages of High Pressure—There are a few other gains resulting from the use of pressure which constitute additional reasons for its use but which are generally not primary reasons dictating such use. For example, rate of chemical reactions increases with the pressure due to increased concentrations and this means greater throughput, or less time for reaction. This is, of course, particularly true of gaseous reactions where the concentration is approximately proportional to the pressure but even with some liquid and solid-phase reactions a remarkable increase in the speed with pressure has been observed. For example, some organic reactions in the liquid phase were observed to increase 5-10 times in speed at 3000 atm. over that at 1 atm.; isoprene and butadiene can be polymerized at room temperature under a pressure of 10,000 atm. However, the application of superpressures above 1000 atm. to increase reaction rates has not yet been applied on an industrial scale.

The reduction in the volume of equipment occasioned by the use of pressure is of value but this alone would not be sufficient justification for use of pressure. Likewise pressure is an aid in certain physical steps that take place in all chemical processes, such as absorption and heat transfer.[7] The use of pressure, by increasing solubility, makes possible certain absorption operations, for example removal of CO_2 from gases by water-scrubbing and CO from gas by absorption in ammoniacal cuprous solutions, which would not be feasible at low pressures. In the

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[5] See Chapter 3.

[6] See Chapters 3 and 14.

[7] See Chapter 2.

du Pont Company's high pressure plant at Belle, West Virginia, the power used to pump the water into the high pressure CO_2 scrubbers is largely recovered by converting the work of high pressure injection into potential energy due to height, by allowing the water to run up the side of a mountain. Figure 2 shows a view

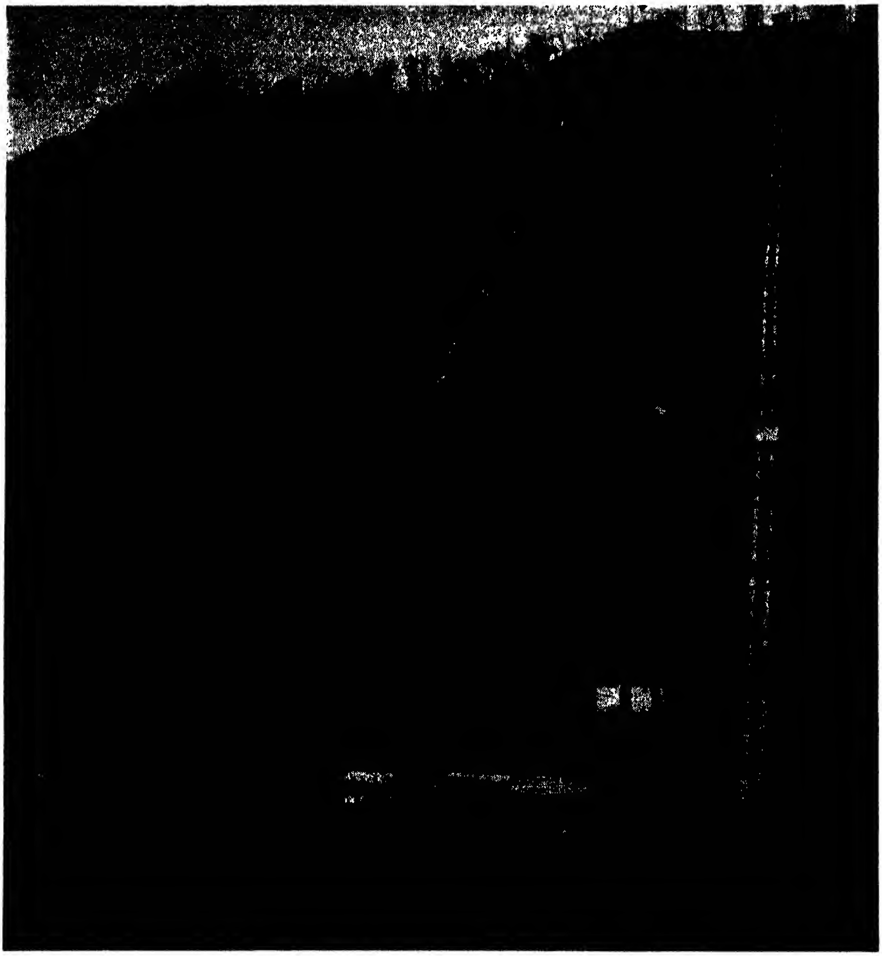

Fig. 2. Du Pont Mountain System of Power Recovery. (Courtesy E. I. Du Pont de Nemours and Co.)

of this interesting "mountain recovery" syste[illegible]e set of pipes carries the high pressure water, charged with carbon dioxide, [illegible]e mountain to the top where the carbon dioxide is released to the atmosphere. The water then returns through the other set of pipes and, due to the head, it builds up a large proportion of the pressure needed to force it back into the scrubbing towers and the pumps need only to boost it the rest of the way.

In some plants the work of water pumping is recovered by means of water turbines. This is a cheaper and more compact system, but recovery of energy is not as good and the escaping gases cause difficulties in the operation of the water wheel.

An interesting case of the use of pressure, where one would predict just the opposite from equilibrium principles, is the dehydro-cyclization of heptane to toluene by the reaction:

$$C_7H_{16} = C_7H_8 + 4H_2$$

In spite of the unfavorable effect on the equilibrium the reaction is carried out under moderate pressures, apparently because of a beneficial effect on the life of the catalyst.

Organic Reactions—In the field of organic reactions one does not have a single clean-cut reaction as in the case of ammonia synthesis and therefore it is not always possible to predict what the effect of pressure would be. So many simultaneous and consecutive reactions are possible and in each case the pressure may affect both the equilibrium and the rate in an unpredictable way.[8] For example in the Fischer-Tropsch process for the synthesis of hydrocarbons from carbon monoxide and hydrogen, the character of the product can be modified in an unpredictable way by relatively small changes in the pressure. Nor is it evident what the effect of pressure is in the hydrogenation of complex substances like coal or petroleum-hydrocarbon mixtures. When hydrocarbons are oxidized at ordinary pressure, the reaction goes almost wholly to CO_2 and water but by oxidizing under pressure it is possible to stabilize intermediate products and thus obtain good yields of liquid products including alcohols, aldehydes, ketones and acids.[9] Though this process has not yet found industrial application it is cited because it illustrates an important effect of pressure which is difficult to predict and which may lead to future applications.

Practically the only clean-cut organic reaction facilitated by pressure is the methanol synthesis reaction:

$$CO + 2H_2 = CH_3OH$$

By suitable choice of conditions this reaction can be made to take place practically to the exclusion of all others. The extent of this reaction as a function of pressure, temperature and proportion of reactants can be fairly accurately predicted from the thermodynamic data. The only other simple reaction between these two reactants is the formation of formaldehyde but investigation of the equilibrium in this reaction[10] has shown that only very small yields are to be expected even at 1000 atm. Many other reactions between these two substances are possible but all attempts to produce any one pure compound have failed. Once the attempt is made to build up compounds with more than one carbon atom, there seems to be no way to control the reaction within narrow limits and a complex product results. This is the case, for example, in the synthesis of the higher alcohols from carbon monoxide and hydrogen.

CATALYSTS

Practically all high pressure syntheses are dependent upon catalysts to bring about a sufficiently rapid reaction to make them commercially feasible; hence it is

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[8] See also Chapter 3.

[9] For production of fatty acids from petroleum, see Chapter 42.

[10] Newton, R. H. and Dodge, B. F., J. Am. Chem. Soc., *55,* 4747 (1933).

appropriate to say a few things about these important agents. At a sufficiently high temperature, most reactions would be rapid without a catalyst but then other conditions would be quite unfavorable. For example, the equilibrium generally becomes less favorable as temperature increases and the problem of materials to withstand the combination of pressure and temperature becomes exceedingly difficult. It is usually essential to keep the temperature under 600° C., at least.

In spite of all the research that has been done on the theory of catalysis there is only one reliable way to determine the best catalyst to use and that is the time-honored method of trial and error. Of course there are certain guides that aid one in the preliminary narrowing down of the field. Certain elements or compounds are generally known to favor certain types of reactions. For example nickel or copper or certain chromites are known to favor hydrogenation, whereas certain oxides like alumina or tungsten oxide promote dehydration but even these very general rules break down in specific instances. There are so many variables affecting not only the activity of a catalyst but also certain physical properties which may be of equal importance. Thus, a catalyst suitable for industrial use must be rugged enough to resist disintegration due to purely mechanical forces, must have long life,[11] and be resistant to heat and to poisons. The development of a catalyst with the necessary physical and chemical properties for a specific case requires many hundreds of purely empirical tests and most companies who are operating catalytic processes have elaborate catalyst testing laboratories.

The specification of the elements or compounds that are active in a catalyst is far from a complete characterization of the catalyst. Physical state may be just as important as chemical composition. For example zinc oxide is a methanol catalyst but the activity depends entirely on the method of preparation and subsequent treatment of the oxide. Some forms of zinc oxide are wholly inactive as catalysts and others will exhibit varying degrees of activity. What may seem to be minor variables in method of treating the oxide—variables involved in the precipitation, drying or heat treatment of the catalyst—may exert an important influence on the properties.

In some cases the active catalyst is a metal and in other cases it may be an oxide or a salt. There is a certain amount of ambiguity in referring to catalysts which may confuse the uninitiated. For instance it is commonly said that the usual ammonia catalyst is a promoted iron oxide. It is true that the catalyst is charged into the reactor as an oxide but before use it is reduced to metallic iron which is the true catalyst. In another case one may speak of a methanol catalyst as consisting of 45 mole % chromium and 55 mole % zinc. This does not mean that the catalyst is a mixture of these elements, for it is actually in the form of oxides which are not reduced to the metal. It merely means that these two elements are present in this proportion.

Most catalysts do not consist of a single element or compound but of a mixture of two or more. For example, most ammonia synthesis catalysts consist largely of metallic iron as the active agent but small amounts of other substances,

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[11] This must be qualified in the case of recent vapor-phase cracking processes used in the petroleum industry, such as the Houdry process, where the life of the catalyst is only a matter of minutes. Such catalysts are re-activated in place by passing heated air through them and elaborate control mechanisms have been developed to control the cycle changes.

often called promoters, are essential for a good catalyst. In this case the promoters are usually basic oxides such as those of the alkali or alkaline earth elements or of aluminum. One common ammonia catalyst is doubly promoted with potassium and aluminum oxides. In the case of methanol, zinc oxide, chromium oxide and metallic copper are definitely known to exhibit catalytic activity but a combination of zinc and chromium oxides is much better than either one alone. In this case the two oxides are used in roughly equal proportions so that there is no clear-cut distinction between catalyst and promoter as in the ammonia case. The properties of a methanol catalyst can also be modified in an important way by the addition of relatively small amounts of other elements. For example, a catalyst containing only zinc and chromium (as oxides, of course) will give substantially pure methanol but the addition of small amounts of alkalies, or of copper or manganese or other elements will lead to the formation of significant amounts of higher alcohols in addition to methanol.

Most catalysts are used in the form of a stationary bed through which the reactants pass and hence they must be in lump or granular form. This form can sometimes be produced without special mechanical means by proper control over the conditions used in manufacture. In other cases it is necessary to compress the powdered catalyst into pellets. In still other cases the catalyst is held on a supporting material which is itself in suitable granular form such as pumice or Alfrax or is impregnated on a powdered material such as kieselguhr which is then pressed into pellets. A recent interesting development in the petroleum industry is a process in which the catalyst is suspended as a very fine powder in the moving stream of the reactants, then separated by mechanical means, reactivated if necessary, and again dispersed in more reactant mixture.

SURVEY OF PRESSURE PROCESSES USED IN INDUSTRY

The number of possible processes which might advantageously be carried out under pressure is very large and this discussion will be confined to a few of the most important ones that are used industrially. These, with some of the important operating conditions, are summarized in Table 1.

The processes in the table are believed to be in actual operation on an industrial scale. Many other reactions have been investigated in the laboratory and on a semi-commercial scale which may be the basis of future industrial processes.

In addition to the chemical reactions listed, there are a number of physical processes in which pressure is a useful tool, as for example in the recovery of helium from natural gas, the manufacture of liquid oxygen, the repressuring of petroleum-producing wells in which the oil production is from a saturated vapor in the critical region and maintenance of the pressure is necessary to continued production, electrolysis of water under pressure, and the use of high pressure steam to explode wood to a fibrous material from which useful products are pressed.

METHANOL SYNTHESIS

This has been chosen as a typical high pressure catalytic process about which to give more detail than was possible within the confines of Table 1.

The reactants, hydrogen and carbon monoxide in the proportion of 2 to 1, may be produced in a variety of ways from different raw materials though only three sources of the gases are believed to be in use at the present time. These three sources are:

(1) by-product gases from the fermentation of corn[12]
(2) by-product gas from carbide[13] furnaces
(3) coal and water.[14]

In the case of (1) the gas is a mixture of CO_2 and H_2 in about equal proportions. Methanol can be synthesized from these two gases just as well as from CO and H_2 but of course water is formed at the same time so that the product is a solution of methanol in water instead of substantially pure methanol. This can be avoided by first converting the CO_2 to CO by passing it over a bed of hot coke where the reaction

$$CO_2 + C = 2CO$$

takes place.[15]

In case (2) the gas is nearly pure CO, a portion of which is converted to hydrogen by means of the water-gas reaction, namely:

$$CO + H_2O = CO_2 + H_2$$

The CO_2 may be removed in a variety of ways leaving a substantially pure hydrogen which is then mixed with the original gas in the proper proportion.

In the case of (3) the coal is coked[16] in ovens and the resulting coke is used to produce blue water gas which is then mixed with hydrogen obtained from the coke oven gas by low temperature separation.

Other possible sources of the two reaction gases are (1) blue water gas from coke, a part of which is converted to hydrogen through the water gas reaction. (2) by-product CO from phosphorus manufacture, (3) coke-oven or other coal gases, (4) petroleum[17] cracking gases and (5) natural gas. In certain localities natural gas should offer a very cheap source of raw material for methanol synthesis. One of the difficulties in such a source is seen by considering the reaction which occurs when natural gas (assumed for simplicity to be methane) is treated with steam and passed over a catalyst, namely

$$CH_4 + H_2O = CO + 3H_2$$

Since a 2 to 1 gas is necessary, either hydrogen must be removed or carbon monoxide added. There are several possibilities for doing this, only two of which will be mentioned briefly. The CO and H_2 can be separated by a low temperature distillation process and the CO added to some of the original gas mixture resulting from the reaction with steam, or some of the natural gas can be burned and the CO_2 separated from the flue gas by suitable means. The CO_2 is then mixed with the natural gas and steam to bring about the net reaction

$$3CH_4 + CO_2 + 2H_2O = 4CO + 8H_2$$

A simplified flow sheet showing only the main features of one process for methanol synthesis starting from coal and water as the raw materials is given in

[12] See Chapter 30.

[13] See Chapter 12.

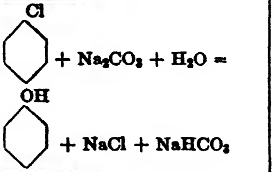
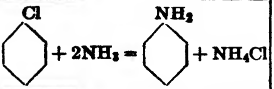
[14] See Chapter 19.

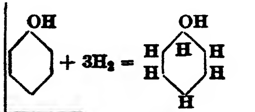
[15] See Chapter 15.

[16] See Chapter 15.

[17] See Chapter 14.

TABLE 1—OUTLINE OF MOST IMPORTANT INDUSTRIAL PRESSURE PROCESSES

Process	*Reaction*	*Temp. ° C.*	*Pressure Atm.*	*Raw Materials*	*Catalyst*	*Phase*	*Notes*
Ammonia synthesis (3)	$N_2 + 3H_2 = 2NH_3$	400–600	100–1000	Coke, air, water, by-product H_2, natural gas	Promoted iron oxide	Gas	
Methanol synthesis (4)	$CO + 2H_2 = CH_3OH$	300–450	100–1000	Coke, water, by-product H_2 and CO, natural gas	Zn and Cr oxides with or without promoters	Gas	
Urea synthesis (3)	$CO_2 + 2NH_3 = CO(NH_2)_2 + H_2O$	200	375	Ammonia and by-product CO_2	Non-catalytic	Liquid	
Higher alcohol synthesis	$nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O$	300–450	200–1000	Same as methanol	Alkalized methanol catalysts?	Gas	Many catalysts claimed. One actually in use is not known. No one pure alcohol can be made. Product is a mixture of primary and secondary alcohols with from 1 to 9 carbon atoms.
Hydrolysis of chlorbenzene		300–350	200–300	Chlorbenzene, diphenyl oxide, soda ash	Copper	Liquid	Diphenyl oxide added in equilibrium amount to prevent further conversion to this by-product.
Ammonolysis of chlorbenzene (1)		190–210	60	Anilin, ammonia	Cuprous salts	Liquid	Phenol and diphenylamine formed as by-products.
Propionic acid synthesis	$CO + C_2H_5OH = C_2H_5COOH$	150–350	100–800	By-product CO and ethyl alcohol	Mineral acids Boron trifluoride	Liquid	No published data on this reaction. A similar reaction between CO and MeOH to give HAc is also believed to be in commercial use.
Methyl formate synthesis	$CO + CH_3OH = HCOOCH_3$	....	350	MeOH and by-product CO	....	....	Step in production of methyl methacrylate.
Higher alcohols from fatty acids	$RCH_2COOH + 2H_2 = RCH_2CH_2OH + H_2O$	350–400	200	Natural fats and oils and hydrogen	Copper, zinc and other chromites	Liquid	Many possible variants of this general reaction.

Production of hexalin (cyclohexanol)		175	....	Hydrogen and phenol	Nickel	Liquid	
Tetralin and decalin production	$C_{10}H_8 + 2H_2 = C_{10}H_{12}$	....	....	Naphthalene and hydrogen	Nickel and copper chromite	Liquid	Decahydronaphthalene produced by same reaction.
Hydrogenation of coal and tar	Complex	400–500	200–700	Coal or coal tar, water, by-product H_2	Mo, W or tin compounds	Liquid and vapor	Fuels and lubricants for internal combustion engines and fuel oil produced.
Polymer gasoline (2)	Polymerization of olefins	200–600	15–200	Unsaturates in cracking still gases or light saturated hydrocarbons	Phosphoric or sulphuric acids on a carrier or non-catalytic	Vapor	The purely thermal process uses higher temperatures and pressures than the catalytic one. When raw material is saturated hydrocarbons, both cracking and polymerization occur in one operation.
Cracking petroleum oils (1) (2)	Complex	500–600	50–70	Various petroleum fractions	None	Liquid	
Iso-octene production (2)	$2C_4H_8 = C_8H_{16}$	150–200	50–100	Butenes	Phosphoric acid	....	Similar to polymer gasoline process but using substantially pure butenes as raw material. Product is hydrogenated to iso-octanes.
Hydrogenation of petroleum (1) (2)	Complex	....	200	Various petroleum products and hydrogen	Metal oxides	Liquid	Can produce a variety of products depending on charging stock and conditions.
Thermal alkylation (2)	Isobutane + ethylene → Neohexane	500–525	200–300	Various light saturated hydrocarbons	None	Vapor	The saturated hydrocarbons are cracked to produce ethylene.
Petroleum reforming (1) (2)	Complex, including cracking, polymerization, isomerization and cyclization	500–600	50–100	Various petroleum fractions	None	Vapor and liquid	Production of more desirable products from less desirable ones (for ex., high octane gasoline from lower octane gasoline) without great change in volatility range.
Synthesis of ethylene glycol	$CH_2O + CO + H_2O = \begin{array}{l} CH_2OH \\ \vert \\ COOH \end{array}$ $\begin{array}{l} CH_2OH \\ \vert \\ COOH \end{array} + 2H_2 = \begin{array}{l} CH_2OH \\ \vert \\ CH_2OH \end{array} + H_2O$	....	....	Formaldehyde, CO, H_2 and water	....	....	Very recent application and no data on reaction conditions available. The formaldehyde is made from methanol by oxidation.

(1) For discussion of the principles of this unit process, see Chapter 3.
(2) For details of the commercial application, see Chapter 14.
(3) For details of the process, see Chapter 8.
(4) For details of the process, see Chapter 30.

Figure 3. The coal is converted to coke and gas in ovens of standard type. The coke is then fed to water-gas generators where a blue gas containing approximately equal volumes of CO and H_2 is produced. This gas contains hydrogen sulfide which would poison the methanol catalyst and cause other troubles later in the process so it is removed at this point by any one of several well known processes,[18] as for example the Thylox process which uses a sodium arsenate solution as the absorbing agent. The gas is then compressed to about 30 atmospheres in 2- or 3-stage compressors and scrubbed with water under pressure in a packed tower to remove carbon dioxide (formed in the gas generators) along with some other impurities. The gas now consists of approximately equal volumes of hydrogen and carbon monoxide and hydrogen is added to adjust the composition to the desired 2 to 1 mixture. This hydrogen is produced from the coke oven gas by a low temperature process in which all the other constituents of the gas are liquefied, leaving the hydrogen which is a non-condensable gas at the temperature (−300° F.) used.

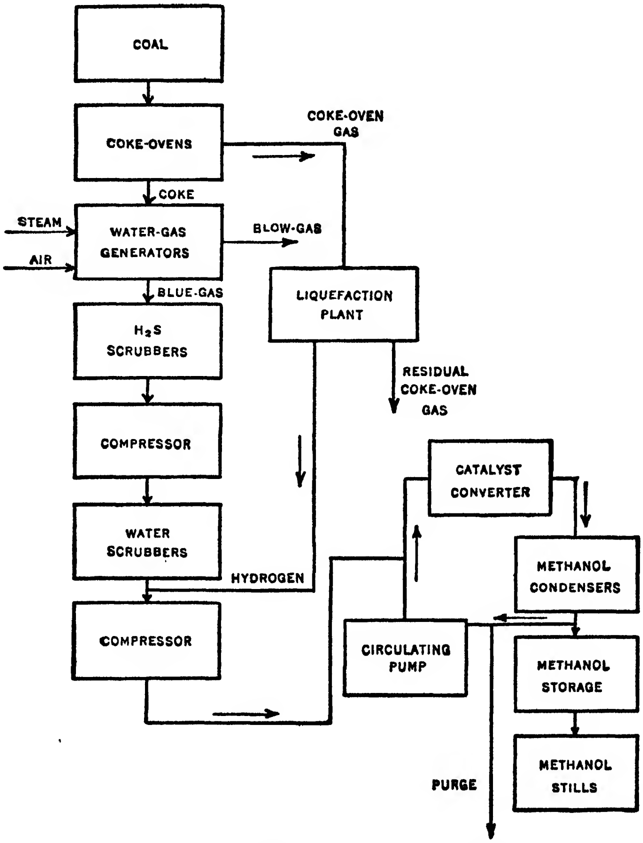


FIG. 3. Simplified Flow Sheet of Process for Methanol Synthesis.

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[18] See Chapter 15.

The purified and compressed gas mixture containing hydrogen, carbon monoxide and small amounts of other gases, principally nitrogen, methane and carbon dioxide, now enters a recirculation system where the synthesis takes place. The gases from the recirculating pump mix with fresh, make-up gas and enter the converter in which they first exchange heat with the hot gases leaving the catalyst bed. In this way the entering gases are heated to about 300° C. before entering the catalyst chamber. This heating is necessary to start the reaction at a sufficiently rapid rate. Since the reaction is exothermic the gases leave the catalyst at a somewhat higher temperature (approximately 400° C.) and the temperature is continually maintained at the proper level by heat exchange between ingoing and outgoing gases. Of course, when a converter is cold after a shut-down, some auxiliary means of heating has to be used to start the reaction.

Fig. 4. High Pressure Compressors in a Synthesis Plant. (Courtesy of E. I. Du Pont de Nemours and Co.)

Depending on the catalyst, temperature, pressure, space velocity and other factors, from 10-20% of the carbon monoxide is converted to methanol in one pass through the converter. By cooling the gases with water in a tubular cooler, the majority of the methanol (and higher alcohols if they are present) is condensed to a liquid and flows to a receiver whence it is expanded to a low pressure storage system. The uncombined hydrogen and carbon monoxide are then recirculated to the converter. Since the make-up gas contains a certain amount of inert gas and since some inerts such as methane are formed in side reactions, a certain proportion of the gas must be continuously purged from the circulatory system to prevent the inerts from building up. In order to avoid too great a loss of active gas through the purge, the inerts in the system are generally maintained at a fairly high figure, of the order of 20-30%. The only disadvantage of this is that it reduces the effective pressure of the reaction.

EQUIPMENT

Compressors—Gas is compressed in reciprocating compressors of the type shown in Figure 4. Both for mechanical and thermodynamic reasons, the compression is done in more than one stage with inter-stage cooling. In general, two stages are used to 25 atm., 3 stages to 75 atm. and above that 4, 5, or 6 stages are common, though as many as 9 stages have been used. Compressors for pressures up to 300 atm. are fairly well standardized. Machines for pressures as high as 1000 atm. have been built but are quite special. Laboratory compressors have been built for 5000 atm. but 1000 atm. is the highest for which any commercial compressor has been constructed.

Compressors are commonly driven by a steam engine or an electric motor. Steam-driven compressors have a steam engine cylinder integral with the compressor and directly in line with a gas compression cylinder. Power-driven compressors may be connected by a belt drive to the motor, or as is more common in the large sizes, a synchronous motor is directly connected to the crank shaft.

High pressure compressors have been built in large units capable of compressing several thousand cu. ft. of gas per minute measured at atmospheric pressure. The power requirement, which may be an important item in the cost of the process, is readily calculated from the usual equation for adiabatic compression with a reasonable allowance for overall efficiency (80-85%).

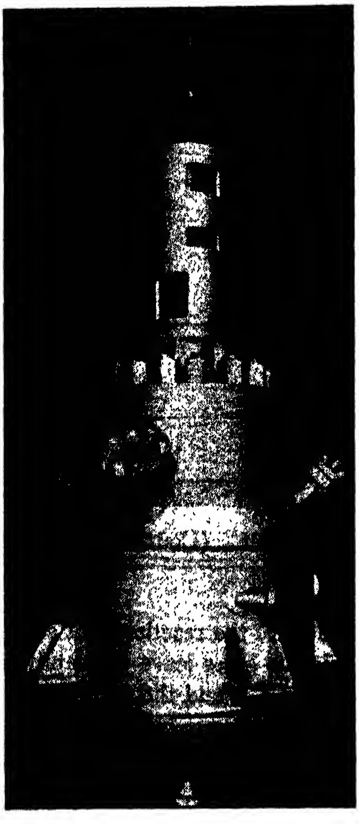

Fig. 5. Autoclave with Agitator. (Courtesy Blaw-Knox Co.)

Pressure Vessels—Vessels for high pressure reaction or storage are of three general types. For pressures up to about 100 atm. the vessel is commonly made of steel plate rolled to a cylinder and welded. The vessels used for batch reactions in which the pressure is simply the vapor pressure of the system at the reaction temperature, are usually known as autoclaves and are commonly equipped with mechanical agitators. Such a reactor is shown in Figure 5. Larger vessels of the same type of construction without stirrers are used in continuous processes such as the various high pressure processes used in the petroleum industry. (See Figure 6.) For higher pressures, such as used in the ammonia and methanol synthesis, the reactors are generally forged from a single ingot of steel. (Such a vessel is shown in Figure 7.) The size of such reactors is limited by the largest ingot that can be produced which is about 225 tons. The largest converters that can be fabricated in this way will produce from 50-70 tons of ammonia per day in a single unit.

Fig. 6. High Pressure Petroleum Cracking Vessel. (Courtesy A. O. Smith Corp.)

The most recent type of construction is the laminated one which consists of wrapping successive layers of relatively thin sheet (about ¼″) around a central cylinder, and welding the circumferential seams. Such a vessel in process of construction is shown in Figures 8 and 9. By this method thick-walled vessels can be built up to withstand very high pressures and larger vessels can be made than from forgings which makes possible larger units with a corresponding reduction in costs. Furthermore, only the inner cylinder need be of a special material to withstand the corrosive action of reacting materials.

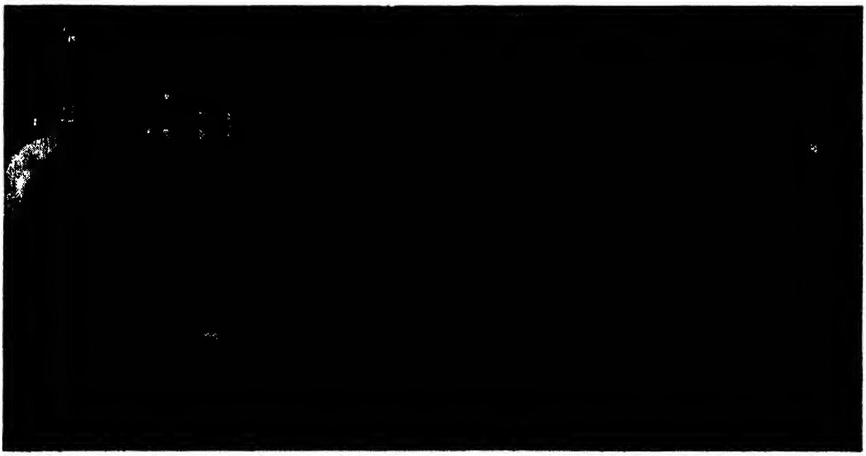

Fig. 7. Forged Steel Reactor for Ammonia Synthesis. (Courtesy Midvale Steel Co.)

All pressure vessels have bolted-on heads and their gas-tightness is assured by the use of a gasket of some yielding material, usually copper or aluminum or soft steel. Typical head constructions using copper gaskets are illustrated in Figure 10. Where steel is used the joint is usually of the line-contact type illustrated in Figure 11. In the older types of head closures it was necessary to initially tighten the head onto the gasket with sufficient force to overcome the

FIG. 8. Two sections of a multi-layer vessel shown after twenty-six layers progressively have been wrapped and welded. (Courtesy A. O. Smith Corp.)

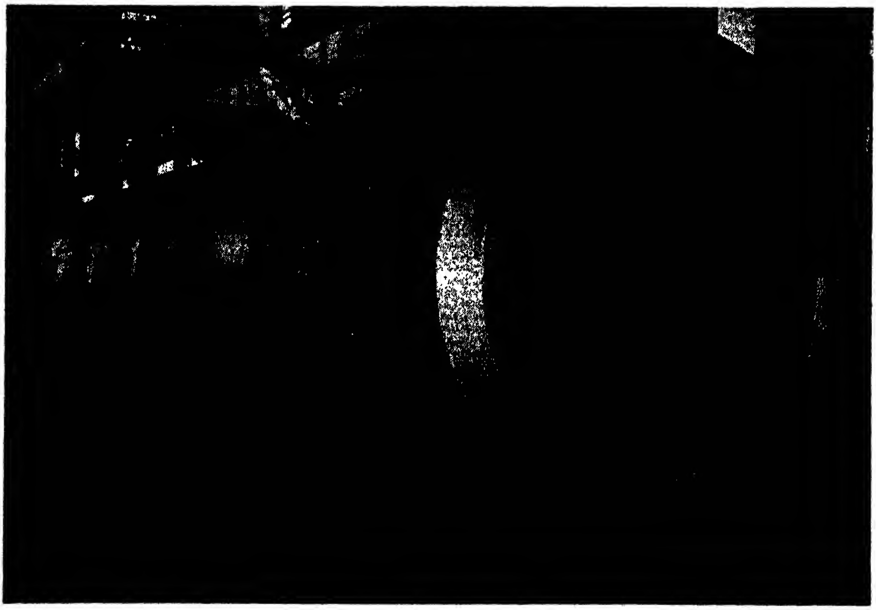

FIG. 9. The end of this multi-layer shell has been machined for the welding groove. This shell has a total wall thickness of 5.3 inches built for twenty-six layers. (Courtesy A. O. Smith Corp.)

total load on the head due to gas pressure and still leave enough residual hydrostatic pressure in the gasket to prevent leakage. This is avoided in the newer types of closures using a floating head which is forced against the gasket by the internal pressure, as illustrated in Figure 12.

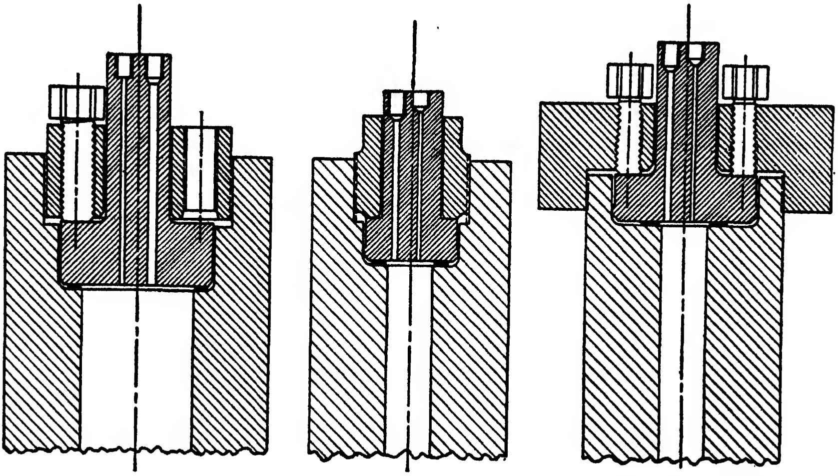

FIG. 10. Types of Head Closures for Pressure Vessels. [Ind. Eng. Chem., *18*, 667 (1926)]

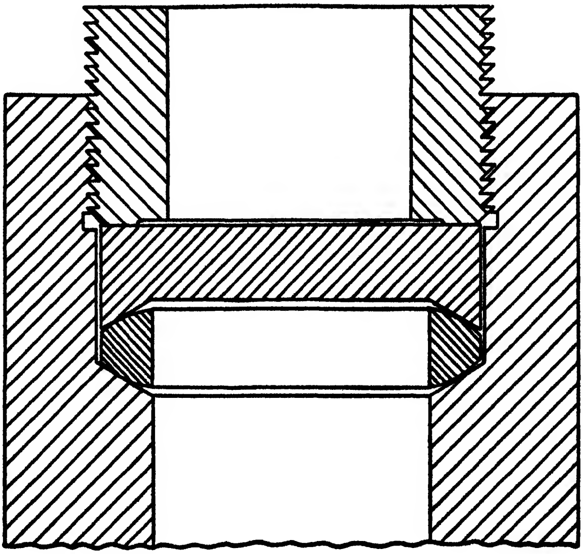

FIG. 11. Lens Ring Joint.

Materials of Construction—For the lower pressures and in the absence of hydrogen, mild steel may be used in the construction of pressure vessels. Hydrogen causes decarburization of mild steel above about 200° C. with resultant cracking along crystal boundaries. For the combination of high temperature, high pressure and hydrogen-containing gases, alloy steels containing chromium, nickel, vanadium, tungsten, or molybdenum and combinations of them are used, a common one containing 1% chromium, 0.2% vanadium and 0.3% carbon. The elastic limit depends on the heat treatment but is generally in the range of 65,000-85,000 lbs. per sq. in. Where severe corrosion is encountered, special alloys high in nickel and chromium must be employed. For the very severe conditions encountered in such a process as the Claude for ammonia synthesis operating at 550-650° C. and 1000 atm., the converters are made of a nickel-chromium-iron alloy containing about 25.5% iron, 12% chromium, 60% nickel and 2.5% tungsten.

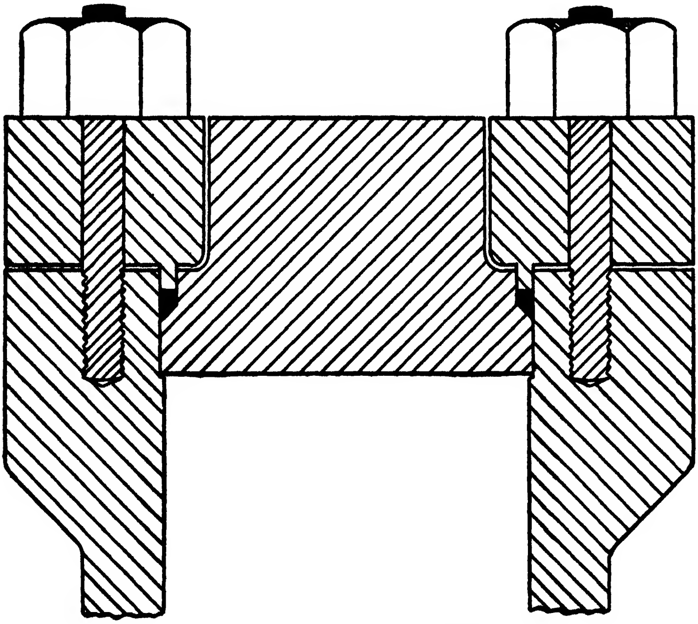

FIG. 12. Self-sealing Closure.

The tensile properties of all steels are little affected by temperatures up to 250° C., above 300° C. a fairly rapid decrease in strength sets in, and above about 400-450° C. the proportional limit becomes very low and the so-called "creep" phenomenon becomes important. This is a continuous elongation that occurs without increase in the stress. An important property of steels to be used at high temperatures and pressures is the creep stress which is defined as the stress that will produce 1% elongation in a certain number of hours, usually from 25,000 to 100,000. In contrast to the ordinary short-time tensile tests, the creep stress can only be evaluated by long-time tests of at least 1000 hours.

Liquid Pumps—Liquid pumps for high pressures have generally been of the reciprocating plunger-type though recently centrifugal pumps have been developed for large rates of flow at pressures as high as 3000 lbs. per sq. in. These are multi-stage pumps driven either by steam turbines or high speed electric motors and there appears to be no reason why still higher pressures cannot be developed if the demand arises. For low and moderate flow rates the reciprocating pump still dominates the field.

Miscellaneous Equipment—Valves, packings, pipe and fittings, pressure gages, flow meters, safety valves and other small items of equipment are not essentially different for high pressure processes from those employed at low and moderate pressures, but little details of design are important and may make the difference between success and failure. The construction must, of course, be heavier and frequently of special steels to secure higher strength without so great an increase in weight. For the highest pressures, seamless tubing is generally used in place of pipe with welded seams. Joints are made with flanges and soft metallic gaskets or the lens ring gasket shown in Figure 11. Fittings may be forged or they may be machined from bar stock. Sight glasses constitute a special problem which has necessitated more of a departure from the conventional designs.

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CHAPTER 5

INDUSTRIAL INSTRUMENTATION

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The scope of this chapter must be arbitrary. It includes only industrial instruments, as against the more scientific laboratory instruments; i.e., instruments, in the former case, are those employed for definite processing conditions, physical and chemical properties, and compositions of materials. The devices described are those that render some or all of the following services to industry: Labor saving; fuel saving; increased production; better quality of product; elimination of "rejects"; uniformity; accident prevention; and minimizing reliance on human watchfulness.

MEASURABLE CONDITIONS

As processes are taken from the research laboratory to the plant, they become industrialized, i.e., they are carried on in standardized production equipment and a determined attempt is made to control variables, with a view to preventing accidents and spoilage and to assure highest quality of output at lowest production cost. These variables, which are of prime importance to the industrial chemist, can be determined, and therefore may be considered as measurable conditions. In their probable order of importance to the chemical industries, these are as follows:

1. Temperature.
2. Humidity.
3. Pressure (or Vacuum).
4. Liquid Level.
5. Flow.
6. Duration or Timing (of chemical process).
7. Rate or Speed (of mechanical parts)
8. Chemical Strength (of processing medium—acidity of bath, etc.).
9. Light, Ultra-violet Irradiation, etc.
10. Voltage, Current Density, Magnetic Flux, etc.

The foregoing list includes only those measurable conditions for which industrial instruments have been designed, developed, standardized, and placed on the market.

PROPERTIES

The industrial chemist strives to conquer variations in processing conditions because he desires that every product meet definite specifications as to purity, physical and chemical properties. Specifications have for many years been checked in laboratories and, as a result, innumerable types of testing instruments have appeared. Laboratory testing instruments are becoming standardized. Many of them have become *industrialized.* To illustrate:

A liquid product must have a definite specific gravity. This property (not "condition") is tested in the laboratory by means of a glass hydrometer. Substitute a rugged steel float chamber, add a temperature-compensation device, connect the float chamber into the outflow of the processing apparatus and the float to a recording mechanism—and the result is a specific gravity recorder.

COMPOSITION

A third large and important field of application of industrial instruments is the measurement and control of chemical composition. From this field we arbitrarily exclude portable analyzers which require manipulation or which are not capable of providing pointer-and-scale indications or chart records.

Two distinct historical sequences have resulted in automatic analyzers. One has been the gradual evolution of fragile laboratory bench glassware into rugged apparatus, with more and more routine operations mechanized, from the taking of uniform samples at the start to the taking of readings at the end. This form of automatization is the mechanization or motorization of previously manual or visual routines. The other historical sequences have been more rapid in every case: not an evolution but the application of continuously recording instruments to continuous methods—or the transformation of a laboratory continuous analysis apparatus into a fully-automatic continuous analysis industrial instrument. The term "analyzer" generally signifies a selective analyzer—an instrument which records one constituent by one selective method, or a duplex or multiplex recorder consisting of two or more fundamental measuring devices assembled into one case so as to produce a plurality of records on a single chart. Though new, this province of automatized analysis comprises a number of fields, more or less overlapping and only faintly corresponding to the formal divisions in college chemistry courses. We discern ten distinct fields in this province—*ten classes of robotized analyzers:*

I. Automatized gas analysis methods in which the percentage of a constituent is measured by measuring a physical property of the mixture, without any chemical reaction being performed. Any physical property may be utilized which is readily measurable or—better still—continuously measurable by an industrial instrument. It must be noted, of course, that the mixture rule limits the application of property-measurement methods to mixtures where the value of the utilized property is appreciably greater or smaller in the gas to be recorded than in any other constituent. Another peculiarity in the use of property-measuring methods of gas analysis is that the different constituents frequently have different temperature or pressure coefficients of the particular property. This may be a source of error, but it also permits analyzing certain mixtures at temperatures where the constituent tested for, displays the utilized property more markedly than do the other constituents. Finally, most of these methods being continuous in their industrial embodiments, the instruments can readily be made to serve as the measuring elements of telemetering systems, or of automatic control systems.

II. Same as (I) but for solutions. Among the physical properties reliably indicative of the concentration of a particular ion, element, or compound in a solution, the most useful are electrical properties. These come under electrometric methods which for reasons of convenience constitute a field of their own. (VIII, below.) Any of the remaining physical properties can be utilized when it can conveniently and accurately be recorded, when the ion, element, or compound tested for has a pronounced influence on the value of the solution's property, and when there is practically no danger of the presence of other ions, elements, or compounds affecting the shape of the curve on which the instrument's calibration is based.

III. Mechanized volumetric gas analysis methods consisting of a single selective absorption or selective oxidation stage for quantitative determination of one constituent of the mixture, preceded and followed by simple automatized washings and other routines. Modern features are designed to assure definite conditions of pressure, volume, temperature, and either drying or saturation; or to compensate automatically for variations in some of these conditions. In large plants the readings obtained from the final gasometer bell of the analyzing instrument are converted into proportional electrical effects and telemetered to centralized control boards at a distance from the points of analysis. Any of these indicating and recording instruments, moreover, can readily be made to serve as the measuring element of an intermittent type automatic control system which, after each cycle of measurement, readjusts various valves and dampers.

IV. Mechanized volumetric methods similar to (III) but comprising two or more selective absorption or oxidation stages—either because the determination of one constituent requires it or in order to measure the percentages of a plurality of gases.

V. Continuous-absorption gas analyzers with pressure-measuring instruments serving as indicators, recorders and telemetering-system transmitters. Since measurement is continuous, the instruments can be supplemented by a wide choice of telemetering or automatic-control systems.

VI. Combination of chemical reaction and physical property measurement.

VII. Inferential analysis by measurements of effects of changes of forms of energy accompanying reactions. Though generalized by the plural, this obviously refers chiefly to temperature measurements in connection with strong exotherms or endotherms. Outstanding example is the catalysis-cell type of CO recorder.

VIII. Electrometric methods of analysis. This field necessarily overlaps others. By usage it includes methods based on the *electrical* conductivity of solutions, but it excludes methods based on the *thermal* conductivity of gases—the former being considered an electrochemical property and the latter a purely physical property. Important as is this field, it has not yet been defined. The electrometric analytical methods which are successfully embodied in industrial instruments, however, may be listed as follows: (1) potentiometric, (2) electrolytic, (3) polarographic, (4) conductivimetric, (5) magnetometric.

IX. Qualitative detection of any or all unknowns. This has not yet reached the practical stage, though a certain measure of success has been reported in the way of spectroscopes equipped with photocells and sets of screens, each screen having a series of slits corresponding to the principal bands or lines of a certain atom or molecule.

X. General quantitative analysis. Complete automatization still is in the dream stage for it would seem to require (even if limited to the inorganic field) an enormous apparatus corresponding to a large laboratory in which all manipulations are automatized (including judicious choice of reagents for obvious reasons such as explosion prevention), and provided either with a multitude of dials or with means of printing on a chart the result in the form of symbols and quantities.

PRINCIPAL PARTS OF INDUSTRIAL INSTRUMENTS

Because of their great variety it is not possible to discuss, in a systematic way, the anatomy of all industrial instruments. Some classes must even be excluded as, for instance, inclined-tube draft gauges, liquid level sight gauges, etc.

Primary Element—In general, there is a part or group of parts known as the *primary or sensitive element,* which responds to variations in the measurable magnitude to which the instrument is applied. The response may be direct, as in the case of a float for liquid level. Or it may be indirect, as in a flow meter, the primary element of which is a "differential producer." From the scientific viewpoint the response of most primary elements is indirect. Many primary or sensitive elements respond to variations not in the measurable magnitude itself, but in one of its effects. Thus, humidity is not measured in industrial practice by weighing the water vapor in a cubic foot of air, but it is satisfactorily measured by its proportional effects on the readings of thermometers or on the length of a hygroscopic element. Similarly, acidity may in some instances be measured by using a sensitive element which responds to changes in electrical conductivity. In like manner, the proportions in a mixture of gases may be continuously determined, and even controlled automatically, by the use of primary elements which measure either the thermal conductivity in, or the specific gravity of, the mixture. Almost all industrial instruments thus start with primary or sensitive elements which make use of practical applications of relations which were discovered in the field of pure science.

Indicating Element—In indicating instruments a second essential element is the *indicating element,* which generally moves over a graduated *scale.* In some industrial instruments or devices, the indicating element is a lamp which flashes on and off, or a gong or bell. In such cases, the instrument is a *detecting* or alarm instrument or device, rather than an indicating instrument.

In recording instruments, the indicating element, actuated by the primary or sensitive element, in turn actuates (1) a moving pen or other producer of a legible record upon a moving chart, or (2) a relay whereby auxiliary power is employed to produce the record.

Controllers—In automatic controllers, in addition to the primary element, a means for the application of sufficient power is required to effect the desired correction. When this means is physically separate from the parts which measure the controlled variable, it is known as the power device or power unit, or by a specific designation such as motorized valve.

In self-operating controllers the primary element itself furnishes the power; in all other controllers an indicating element is made to actuate a *relay* whereby the application of pneumatic, electrical or other form of power is governed. In some power systems a first and comparatively delicate relay actuates a second and more rugged relay.

Kinds of Instruments—Apart from other methods of classification, it may be useful to supply brief information on some of the "kinds" of industrial and other instruments. The arrangement is alphabetical and the word *instrument* is left out after each heading:

Balancing. A measuring—but not necessarily an indicating—instrument employing the null method of measurement, wherein one effect of the magnitude to be measured is manually or automatically balanced by a calibrated and adjustable effect of like kind and opposite direction. An indicating element is employed to show a state of balance and also, in some cases, to measure the excess of either effect over the other. Examples: equal-beam scales; null-method pressure gauges, tachometers, potentiometers, etc.

Checking. (1) A specialized form of testing instrument, i.e., for occasional or intermittent, not continuous, use. (2) An instrument in continual use for managerial "checking," as of employees' in and out time, etc.

Controlling. An instrument or system (generally the latter) which automatically controls, corrects, governs or regulates (1) the processing, working or storage condition, or (2) the physical or chemical property of matter, or (3) the proportioning to which it is applied. Generally used continuously and permanently installed.

Counting. An instrument that counts discrete entities, such as revolutions, strokes, etc. Examples: A hand counter for shaft revolutions, or an "electric eye" for counting articles traveling along a conveyor.

Curve-drawing. A form of recording instrument, producing a continuous record of a variable magnitude.

Cycling or Coordinating. The designation cycling "instrument" is seldom used in industrial practice. A cycling controller (also known as a cycle controller, program controller, time-operation controller, etc.) is a mechanism embodying (1) one or more clockworks and (2) means for automatically performing predetermined operations at predetermined times in proper sequence, according to either (1) a definite schedule in which all times are fixed or (2) a flexible schedule in which certain times depend on states, stages or conditions. The timed operations may be sudden, as opening or closing valves, or gradual, as in the case of a drying schedule or curing cycle.

Detecting. A signaling instrument or device giving merely a yes or no indication, usually visible (when audible it becomes an "alarm" instrument).

Indicating. (1) An instrument that shows what the value of the measurable magnitude to which it is applied *is* at the time that it is read (or what it *was* shortly before, allowing for lag). Examples: a Bourdon gauge, a liquid-in-glass thermometer, a boiler gauge glass. (2) A detecting instrument giving a yes or no indication without assigning a value, but provided with a visible indicating element. Portable as well as fixed forms are *industrial* so long as the purpose and construction relate to the plant rather than the laboratory.

Integrating. (1) An instrument that automatically performs the mathematical operation of multiplying quantity-rate by time to give total quantity; or a meter which directly registers the total quantity, as of a fluid in units of volume, or of a granular material in units of weight, or of electric power in kilowatt-hours, etc. Reserved for instruments and meters applied to variables, not generally applied to counters. (See Counting.) (2) In photometry, an instrument that performs a *directional* summation of values to give "mean spherical candle power."

Measuring. Any instrument capable of assigning a value to any measurable magnitude (condition, property, effect, etc.). Examples: a foot-rule or a wave-length spectrometer, a grocer's scale or a geodetic torsion balance. Not, as a rule, applied to counting instruments and devices.

Metering. In general an integrating instrument (see Integrating). Special types are maximum-demand meters, etc.

Recording. Any instrument, industrial or scientific, which furnishes a time graph (generally on a moving chart) of the value of the measurable magnitude to which it is applied. It embodies an indicating instrument the indicating element of which (pointer, pen-arm, light-beam focused on sensitized paper, etc., etc.) traces the "record" which may or may not be a "curve." The record is permanent and therefore shows what the value of the measured magnitude *was* at a previous time. The record may be continuous or intermittent. One recording instrument may be applied to several measurable magnitudes.

Registering. A form of indicating instrument provided with means of registering maximum or (sometimes *and*) minimum values, such registering element "staying put" until manually displaced. Examples: a maximum-registering thermometer, a cylindrical tire pressure gauge. (Note, however, that in a meter the mechanism having an arrangement of numerals, etc., which is observed when "reading the meter" is known as the register.)

Regulating. See Controlling; but note that the term *Controller* (which applies also to motor-starting devices, automatic scheduling devices, etc.) is broader than *Regulator* which applies only to devices for controlling the value of a condition, property, etc.

Signaling. An indicating, recording or controlling instrument provided with means for visible or audible signaling at predetermined and usually adjustable "points" or values of the measurable magnitude to which the instrument is applied.

Testing. Implicitly a non-industrial instrument, not permanently installed on a piece of equipment but kept in the laboratory (or taken out on the job) and used as the occasion arises.

Timing. (1) A time-measuring instrument or timepiece. (2) A form of recording instrument, as an operation recorder. (3) An alarm or signaling timepiece which may be set. (4) A controlling instrument which causes an operation to be performed automatically at the end of the period of time for which it is set, such times being ordinarily related to the manual setting operation, but in certain forms to a state, stage or condition independent of the manual setting. (Elaborate forms of industrial timing-controlling instruments are preferably called cycling or coördinating controllers.)

Totalizing. (1) Any counting instrument or device. (2) Any integrating instrument.

PRINCIPAL PROPERTIES OF MEASURING INSTRUMENTS

Accuracy—That industrial instruments are "less accurate" than scientific instruments is an unwarranted generalization. In the first place, the only accurate instruments are the counters, operation recorders, etc., dealing with units. There is no such a thing as absolute accuracy in the instrumental measurement of magnitudes such as temperature, pressure, or rate. Since the function of a measuring instrument is to assign to a measured magnitude a numerical value, i.e., a mathematically-usable quantity, it follows that "accuracy" is the relation between the true value (of the magnitude) and the obtained value (of the quantity). It also follows that *Error* is the difference between the values of the magnitude and of the quantity. The true value, of course, is a quantity obtained by means of a "more accurate" instrument—even when it is represented by a tangible standard of reference such as a precision weight

—for this weight has been certified by means of "still more accurate" instruments, but not by "absolutely accurate" instruments.

Accuracy as defined in the foregoing is the accuracy of an instrument at only one point on its full scale, as determined by comparison against a standard. It is termed the *Point Accuracy.* It is not the important property known as *Intrinsic Accuracy* which is defined as the extent or closeness to which the readings (note the plural) of the instrument approach the true values.

Accuracy is usually expressed in terms of the *Limit of Error* which is the maximum error by which the readings will depart from true values. This limit of error, in turn, may be expressed in several ways. Of these, the preferable one is "percentage of scale range."

The measuring property known as *Precision* is relative: a precision instrument is one that has a relatively long scale for a relatively short range.

Inaccuracy of an instrument is caused by features or factors in the instrument itself, not by conditions of use. Its principal causes are: (1) imperfect material, as variation in bore of a glass tube, etc.; (2) unavoidable physical phenomena such as capillary attraction, etc.; (3) imperfect construction which cannot be improved, such as the finite width of knife edges or points, etc.; (4) imperfect construction which can be improved, such as excessive friction, excessive lost motion, incorrectly cut cams, etc.; (5) unavoidable or partly unavoidable properties of materials, such as the aging of glass and permanent magnets.

Sensitivity—This important measuring property is broadly defined as the response of an instrument to changes in the measured magnitude. The intrinsic sensitivity of an instrument is not to be confused with its sensitivity under conditions of use that can readily be controlled by the user. The practical meaning of sensitivity undergoes inevitable changes when applied to such different instruments as Bourdon gauges, vernier-dial potentiometers, photometers, equal-beam scales, viscosimeters, vibrating-reed tachometers, pyrometers, etc. The following applies only to indicating instruments designed for measuring variables.

The sensitivity of a measuring instrument is the response of its indicating element to changes in the measured magnitude. The sensitivity of an *industrial* indicating instrument is the readily observable displacement of its indicating element caused by changes in the measured magnitude. Unit Sensitivity is the value of the change in the measured magnitude which will cause a change of (1) one milliradian or (2) one scale division or (3) one millimeter on the scale of the instrument—depending on the field of measurement concerned. Ultimate Sensitivity is the value of the change in the measured magnitude which will cause effective motion of the indicating element of the instrument.

Variance is a term used to represent the amount by which the readings of an instrument vary in successive indications of the same value of the measured magnitude. Variance is due principally to (1) backlash or lost motion; (2) friction; (3) changes due to the stress-strain relation of springs in the force-resisting or restoring element of the instrument; (4) changes in the distribution of parts, as variation of position of pivots in bearings or variation in the amount of liquid retained on wetted surfaces; (5) the immediately preceding history with respect to extent and speed of displacement and other phenomena. Variance due to friction can be partly eliminated by tapping the instrument just before taking a reading. Variance due to other causes can be kept at a minimal value by proper maintenance and proper handling.

Often, when a measured magnitude remains constant, the instrument reading may change due to the effects of changes of pressure, temperature, humidity, and similar environmental variables. Correction factors can usually be applied to compensate for these sources of errors.

Sticking—This is the term which denotes that the indicating element does not move without an appreciable change in the utilized effect. This term may also be used to designate the amount of effect required to cause motion of the indicating element, in which case it is expressed as *ultimate sensitivity*. Thus a pressure gauge which requires a change of ±5 lbs. to cause its hand to move at all has an ultimate sensitivity of 5 lbs.

Lag is a term denoting slowness of response of the indicating element, without implying, however, that the indicating mechanism sticks. The "slowness" is relative; a sluggish oscillograph would be considered a rapidly-responsive recording thermometer. True lag follows a logarithmic-decrement law. It is caused by phenomena such as heat transfer at the measuring element—not by indicating-mechanism friction—and is commonly known as "thermometric lag." "Damping lag," on the other hand, is artificially introduced in the indicating mechanism, and it generally has nothing to do with the "true lag" of the primary element. True lag can be altered by changing portions of the measuring system; damping lag, by modifying the damping means which affects the indicating mechanism (or by replacing such damping means when detachable).

Damping is that property which minimizes the time required by the indicating element to come to rest at a new value after a sudden change, but without affecting accuracy. When the pointer (or pen) of an instrument comes to rest only after a series of oscillations, the instrument is said to be "underdamped"; and it is said to be "overdamped" when the indicator approaches the final reading, without actually passing that point, in a period of time capable of being reduced. In general it is desirable to have the movement slightly underdamped, in order that its free swing may give assurance of freedom from sticking. For recorders, the damping requirements vary with the "speed" and other desired characteristics.

"Critical damping" is that obtained when reducing the amount of damping would result in oscillations and increasing it would increase the lag. A "deadbeat" movement is critically damped.

Damping lag is seldom objectionable in indicators. In recorders it may be objectionable when the record must show transients; in controllers it is a factor seriously affecting the mode of control.

Readability—This important measuring property is a combination of (1) general factors such as size of instrument; length of scale; length, width, and sharpness of scale divisions; size and legibility of graduation figures; visibility of indicating element; absence of eye-confusing markings or reflections, etc., and (2) specific factors such as minimization of parallax effect in certain forms of indicators.

Drift connotes *gradual* changes. Some authorities use it to denote that an instrument's indications of the same value change "with age"; others define it as the difference in an instrument's readings before and after undergoing a specified test—generally a form of "accelerated aging" test.

From the foregoing, it is apparent that all measuring properties may be divided into "passive" and "active," the former determinable by inspection, the latter by actual test. Figure 1 represents portions of two dial form instruments of identical size and range (say, an imported aneroid barometer at the left and a rugged American-made power-plant barometer at the right). When shown as a slide in lectures, this always provokes discussions. The reader may well pause to consider the questions he would put to the salesmen offering these two instruments if he were a purchasing agent.

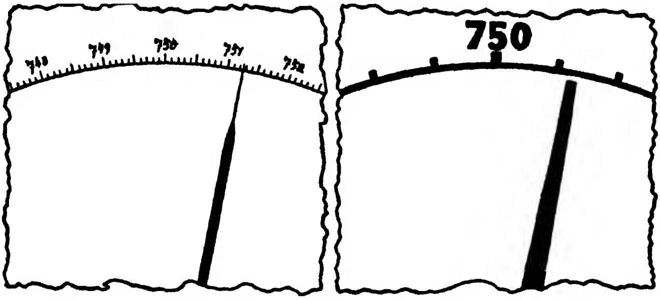


FIG. 1. Illustrating passive measuring properties.

MEASURING PROPERTIES OF RECORDERS AND METERS

Measuring Properties of Recorders—Although the foregoing discussion applied specifically to indicators, much of it applies also to the great majority of recorders—those which, being employed to record variations (and not merely running and idle time, etc.), have a measuring system corresponding to that of an ordinary indicating instrument. It applies especially to direct-acting recorders (see Table 1).

Relay Type Recorders. An outstanding characteristic of relay type recorders is that the measuring element is entirely relieved of the function of moving a pen or other marking element across a chart. This work is done by a servomotor or power device commanded by the measuring element, as in automatic control systems. Power for driving the marking element being derived from an external supply, the measuring element may be constructed to have any degree of accuracy characteristic of its type. This makes possible the application of the zero-reading method in which the relative position of the fixed and moving parts always is the same at the time of actually performing measurement, so that geometrical configuration of parts does not affect the proportionality and some serious sources of error are eliminated.

Chart Forms. An industrial recording instrument produces records on either a round chart with substantially polar coordinates or on a strip chart with substantially rectangular coordinates. An individual instrument cannot be converted from one to the other in practice; but whichever form of chart is desired, either a direct-acting recorder or a relay recorder may be found which uses it. At this writing, however, the majority of relay recorders are strip-chart instruments and the majority of round-chart instruments are direct-acting recorders.

On the round chart, the scale length is necessarily less than the radius. Moreover, since the spaces at the center and at the edges cannot be over-minimized, the scale length of a small-size round chart is not much more than half the radius while in a large-size round chart it may be three-quarters of the radius.

On a strip chart, nearly the whole width of the paper is available for the scale of measured values. Therefore, a strip chart—and a wide one at that—is preferred where the measured magnitude is normally so *steady* that the full sensitivity and accuracy of a high-grade measuring mechanism may be used. In many industrial applications, where considerable damping is essential to prevent blurred records, small round-chart recorders often prove just as satisfactory.

For statistical work, as in taking time-operation records of processing equipment, a wide record is a useless luxury and "miniature" records can serve the purpose. For measurements upon whose precision monetary transactions are directly based it always pays to specify the most "open-scale" strip-chart recorder.

TABLE 1—CLASSIFICATION OF RECORDING INSTRUMENTS

Class	*Type*	*Variety*
Direct-acting Also known as direct-deflection, self-operated, etc.	Direct-writing	Ink in pen Stationary reservoir Photographic Stylus, etc.
	Intermittent-marking	Dotting Thread Ribbon Smoked-chart Spark
Relay	Electrical (contact) High-frequency electrical Mechanical Photoelectric Electronic	In this class the varieties do not depend on the type of relay, most of them being possible with any of the five types

Measuring Properties of Meters—The term "meter" here denotes an integrating instrument. Furthermore, although an ordinary counter integrates (i.e., totalizes discrete entities), the term meter here applies only to instruments capable of integrating continuous-series magnitudes, or "variables." The commonest forms of meters are the gas, steam, water, electricity and other commercial meters in which a counter is driven by a rotating, oscillating or reciprocating primary element.

Theoretically, the accuracy of measurement is independent of the quantity-rate or "load" (within the capacity of the instrument) but it is as impossible to design a usable integrating instrument that does not consume energy, as it is to design a perpetual motion machine. In practice, therefore, the performance of work must be taken into account. It leads to a classification of all integrators into two divisions:

1. "Positive"—Metering instruments the primary elements of which are positively operated by successive quantities and which positively operate the counting train. Examples: wet drum gas meters, water meters in which a chamber is filled and emptied, etc.

2. "Inferential"—Meters the primary elements of which do not isolate and count separate quantities, but operate by virtue of physical laws or empirically determined relations. Examples: rotating disk watthour meters, turbine liquid meters, conveyor scales, etc. Most electricity meters (practically all in commercial service) are inferential meters.

The accuracy of an integrator with a positive element, at normal loads, is not necessarily affected by the rate or by such friction as manifests itself in practice. The accuracy of an inferential integrator is affected by such factors. It is obvious that below a certain hourly capacity for each meter, all meters with inferentially driven counters begin to show friction and other energy-consumption errors, until at extremely low rates (light loads) the utilized effect becomes so weak that the counting train stops and the meter ceases to register at all. (This is true even of electricity meters with friction-compensating coils.) It is also obvious that when the rate or load increases beyond that for which the meter was designed, the meter will "race" and probably register inaccurately, not to mention the risk—and at excessive overloads the certainty—of damaging most meters.

Characteristic Curve. The relation of load to accuracy of registration constitutes, therefore, one of the most important characteristics of inferential meters. It would be the most important were it not for modern refinements that have reduced inaccuracy of inferential meters at light and heavy loads, and made them as dependable as positive meters. This relation, known as the load characteristic curve, is hardly less important nowadays in the case of inferential meters than in the case of positive meters. The ideal curve, load *vs.* registration, is a perfectly straight 45° line starting from the origin. The ideal curve, load *vs.* error, is a perfectly straight line coinciding with the load axis. It is closely approximated by positive meters from very light (but not zero) load to 50% overload or more and sometimes fairly close to the physical destruction point. It is closely approximated by modern inferential meters but only within the upper part of the load range, determined by the size of the meter itself or of its primary element.

Both the inferential fluid meters and the electricity meters show considerable errors at extremely light loads—especially the fluid meters (in general).

In the last analysis the curve depends less on whether a meter is positive or inferential than on the particular type, make, model and even on the condition of the individual meter.

PERFORMANCE OF AUTOMATIC CONTROLLERS

Basic Requirements for Automatic Control—Although industrial chemists are becoming increasingly interested in multiplex controllers which simultaneously control a number of processing conditions, space limitations require that the following discussion be limited to single-measuring-system controllers. Every automatic controller or automatic-control system must necessarily include (1) at the "beginning," a means of measuring the controlled variable; (2) at the "end" an operative means of increasing or decreasing the value of the controlled variable; (3) in between, a means whereby the measuring system *commands* the operative means.

Since no controller can be better than its measuring element, much of what has been said in the foregoing sections on measuring instruments applies here with even greater force. On the other hand, some desirable properties of measuring instruments need not be possessed by the measuring systems of controllers. Again, all controllers are identified with their applications to an extent that does not hold in the case of measuring instruments. An indicator or a recorder merely reports conditions, as would a subordinate sent to look over a situation; a controller takes action, as would an alert executive to whom reports are submitted. All controllers are active, operating devices, to be judged by active performance.

The proper performance of a controller depends, as does that of a manager, on the correctness and timeliness of the information it receives, and on the limits within which its power may be exercised. A float-type liquid level recorder may be installed on almost any chemical process tank big enough to accommodate its float; but an automatic level controller cannot raise the level in the controlled apparatus if the supply is cut off or if the rate of discharge exceeds the rate of supply. Summarizing, we lay down the basic requirements for automatic control of processing conditions in industry:

1. The condition to be controlled must be measurable.
2. The primary element of the automatic controller must be suitable for the measurement involved and must be properly installed.
3. The power device commanded by the control instrument must control an adequate supply.
4. The measuring means must command the corrective means effortlessly, i.e., without having its own measuring properties impaired.

Obvious and simple as are these basic requirements, they are sometimes lost sight of in the maze of engineering details that have to be taken into account in designing intricate installations.

Ordinary self-operating controllers, i.e., those combined with valves, cannot strictly meet the fourth requirement, but the effort exerted by their combination measuring-and-operating elements is minimized by the use of balanced valves, etc., and their applications still outnumber the applications of all relay control systems. The most important process-control applications, however, require the use of relay types, some of them with elaborate amplifying systems, whereby the moving element of the measuring system is altogether free from mechanical drag or electrical attraction-and-repulsion effects.

Control Sensitiveness, Speed, and Range—In no case can a controller react to a smaller deviation than the value of its sensitiveness. But this does not mean that a controller effectively sensitive to a given amount of change in the controlled condition will necessarily be capable of controlling this condition within limits of departure equal to the value of such sensitiveness, for in most cases the installation does not meet all of the four requirements stated above. Even when these requirements are satisfactorily met, the record of the controlled condition may show peaks and valleys several times greater than the total deviation which causes effective action at the point of control. When such installations are analyzed it always is found that the causes of unsatisfactory control involve time elements—lags and delays. There never is any exception. Moreover, it always is possible to split up all time factors into those inherent in the automatic controller and those belonging to the controlled apparatus—"the application." Instrument time factors, being determined by the design and construction of the automatic controller, are predictable. We may therefore lump them all into the expression "controller period." Application time factors vary with the individual pieces of equipment on which a number of controllers (all alike in their period) will be applied.

The *controller period* is generally divisible into as many components as there are elements in the automatic controller. In an electrical controller some of the components would be negligible but others might be considerable: swing of galvanometer pointer, definite regular period of depressor-bar or similar mechanism, time for motor and rack-and-pinion device to change opening of controlled valve, etc.

The period of a well-designed automatic controller in good condition should always be the same for a given amount of sudden deviation from normality. Otherwise, close automatic control would be more or less a matter of chance. But this brings up another fact: certain components of the total period of a controller may be variable. We are chiefly concerned with those that are functions of the amount of departure from normality.

In the case of all controllers with primary measuring elements that do not respond instantly, there always is a component period due to measuring lag. It is impossible to obtain "close" control or "stable" control with a system having a "slow" measuring element. *"Dead times mean dead zones."*

"Droop." The character of the demand factor largely influences the selection of a controller. If the demand is constant, the condition to be controlled will be easier to control, because only the disturbing factors will have to be taken care of—and frequently their effects can be reduced by other means than the performance of an automatic controller.

Where the demand is intermittent, the controlled condition will generally show sudden departures from normality at every changeover point, and it will always *tend* to settle down to *different values* for maximum demand and minimum demand. Application factors are important, then, because they determine to what extent the rate of supply for low demand differs from the rate required to maintain the condition at normality under full demand. When this difference is considerable, the controller should be of one of the "droop-correcting" or "automatic-reset" types which automatically accommodate to the demand the normal position of the supply valve or other operated device.

In general it is difficult when planning a control installation to translate the supply requirements (heat units, current, moisture, fluid flow, etc.) into terms of ratio of valve travel (or other corrective action) to extent and rate of deviation from normality. Therefore it usually is desirable not only to be able to have at one's command from the start a certain amount of motor torque, piston travel, diaphragm-motor force, etc., but to be able to regulate within wide limits, after the controller has been installed, the extent of such corrective action for a given departure from normality. This is especially desirable in the processing industries and, in general, wherever the supply (of heat units, current, etc.) must meet a variable demand.

The Mode of Control—In the foregoing we dealt chiefly with the relation of extent of corrective action to amount of departure from normality. Among others of the same family are the following:

1. Relation of time-rate of corrective action to amount of departure.
2. Relation of extent of corrective action to time-rate of departure.
3. Relation of time-rate of corrective action to time-rate of departure.

These control characteristics largely determine the suitability of a controller for a particular control application.

But the performance of a controller depends also on controller period and application lag; and each of these factors is frequently a variable. Therefore, actual performance of a controller is determined not only by its ratio characteristics but by other factors. The number of possible combinations is infinite and the analogy of a controller to a human being comes to mind. The "performance behavior" of a controller, which we term its mode of control, is determined not only by its range, by its differential setting and by its characteristics, but by other factors, both inherent and external. There are some thirty distinct classes of modes of control, and an indefinite number of grades without sharp divisions. It is well to give thought to these "behavior patterns" not only when selecting a controller but when adjusting it—*and* the controlled apparatus—after installation.

FUNDAMENTAL ELECTRICAL ELEMENTS

Since all classes of industrial measurements (even plain dimensional gauging) can be performed electrically, and since electrical methods are the only practicable ones in many chemical applications, a brief discussion of electrical measuring elements common to all these fields will save numerous needless repetitions.

While the mechanical construction of an electrical instrument is generally simple, the mechanism is comparatively delicate, requiring careful handling and subject to adjustment and repair only by skilled electrical instrument men. In many industrial measuring instruments the actuating and restoring forces are derived from a single element of the mechanism (such as a Bourdon tube), but in electrical instruments the two forces necessary to a definite measurement are almost universally derived from separate sources.

Electrical instruments are particularly sensitive to temperature changes; for not only does temperature affect the lengths of mechanical parts and the characteristics of springs, but also the resistance of electrical circuits. Fortunately, it frequently is possible to provide nearly complete compensation for temperature effects.

A further characteristic of electrical measuring devices lies in the fact that they may be both productive of, and sensitive to, stray electrostatic and electromagnetic fields. This makes it important that in the use of electrical instruments due precautions be taken as to the electrical and magnetic conditions existing in the immediate neighborhood of the measuring equipment, and the proximity of adjacent instruments.

Classifications—There are several ways in which electrical instruments may be classified, and each classification has its use. One system of classification is based on the degree of care and expertness which they require; and this is in almost direct proportion to the precision of the results which may be expected from them: (1) delicate scientific instruments, (2) electrical laboratory instruments, (3) portable testing instruments, (4) switchboard instruments which require some care and occasional checking of accuracy, and finally (5) commercial instruments which are supposed to serve uninterruptedly for years without maintenance.

Another important grouping classifies an instrument as (I) Indicating, (II) Recording, (III) Integrating, or (IV) Controlling. Still another classification of electrical instruments is based on what they measure or determine. Some of these measurable variables are:

Current
Electromotive force
Potential difference
Power
Energy
Frequency
Volt-amperes
Reactive component
Power factor
Phase angle
Synchronism
Wave form
Resistance
Inductance
Capacitance
Impedance, reactance
Magnetic field strength
Flux density
Permeability
Hysteresis (iron loss)
Misc. radio

Basic Principles of Electrical Instruments. Enormous as is the number of purposes to which industrial electrical instruments are applied, however, the numerous utilized effects fall into only four groups:

(1) electromagnetic
(2) electrostatic
(3) electrothermal
(4) electrochemical

Thus only four basic principles of electrical measurements are employed in all industrial electrical instruments. A complete instrument may employ more than one principle but a measuring element or "movement" can only belong to one of these four classes.

In the majority of instrument movements the actuating torque is opposed by a restoring force whose value varies with the deflection of the pointer (or equivalent element). In direct-deflecting instruments a balance between the two forces is automatically obtained by the moving element changing its position under their influences until their respective turning moments are equal and opposite. In zero-reading instruments, the moving element is restored to a fixed reference position by a counter-influence varied manually or through some other outside agency, and the deflection necessary to produce the required restoring force is determined from a suitable scale. The closest similarity to non-electrical instruments is found in electrical measuring elements depending wholly on gravitation for the restoring torque: gravity-control movements are comparable to "primary" or "standard" pressure-measuring instruments employing liquid columns or weighted plungers to oppose the measured pressure.

The number of electromagnetic instruments in use vastly exceeds those of all other classes combined. They are classified into (1) for d.c. only; (2) for both d.c. and a.c.; (3) for a.c. only. The following discussion is based on this three-fold division but—in order to avoid repetition—it also covers movements other than electromagnetic.

Elements Operable on Direct Current Only—Most of these are of the permanent-magnet moving-coil (or d'Arsonval) type shown schematically in Figure 2 and diagrammatically in Figure 3. This movement is found in practically all portable pyrometers, etc. It consists essentially of a rectangular coil of fine wire pivoted on jeweled bearings and free to rotate in the annular space between the soft iron core and the pole pieces of the permanent magnet. Two spiral springs serve the double purpose of conducting the current passing through the coil and of providing a control force. Since the actuating force in such an element is dependent upon the product of the fixed field by the movable field, it is possible by providing a relatively powerful permanent magnet to obtain force sufficient for measurement purposes by the expenditure of a negligible amount of power from the measured circuit.

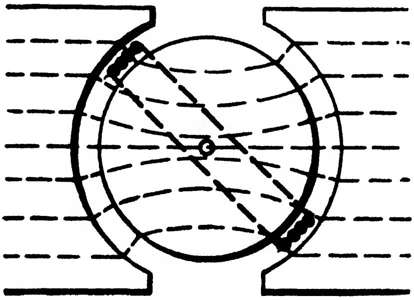


Fig. 2. Diagram of Lines of Force in the Moving Coil Galvanometer.

Elements Operable on Both Direct and Alternating Current—These may be classified as: (1) moving-magnet; (2) electrodynamic; (3) thermal; (4) electrostatic.

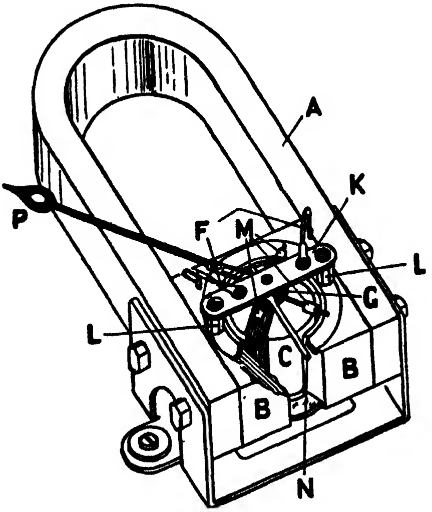


Fig. 3. Construction of the d'Arsonval Type Galvanometer.

In the a.c.-d.c. type of electromagnetic element both the main field and the field produced in the moving part perform their reversals simultaneously, so that a definite and positive torque is produced, having a value which bears a distinct relation to the effective value of the measured current. With direct current flowing in the windings of such instruments a definite measurement is of course obtained, but in some forms it is found that the calibration on direct current differs slightly from the a.c. calibration.

Moving-magnet instruments may be considered as—(1) Solenoid form, in which an iron plunger free to move along the axis of a solenoid takes up a position representative of the value of current flowing; (2) Magnetic vane form, in which a relatively small vane of magnetic material tends to place itself parallel to, or in the most intense portion of, the field of a coil carrying the measured current; (3) Repulsion form, in which two pieces of iron placed within the field of the measuring coil, becoming similarly magnetized, repel each other and tend to move farther apart. Instruments of the moving-magnet type, while usually intended for a.c. measurements, can be employed on direct current as well. Owing, however, to the magnetization characteristics of most irons, the d-c. indication of such an instrument may be affected by its previous magnetic history. Therefore, moving-magnet instruments should not be used for precise d-c. measurements unless definitely guaranteed suitable. Note however that the most sensitive galvanometers (10^{-12} amp., 10^{-9} volt) are of this type.

Electrodynamic Elements. These utilize Ampère's discovery, that two conductors carrying electric current act upon each other with a measurable mechanical force. In electrodynamic movements two or more windings carrying the current or currents to be measured react in such a way as to produce a torque (or thrust). This is measured either by providing, and determining the value of, an opposing torque to bring the moving coil to a standard position of reference, or by measuring the deflection of the moving coil against a varying control torque. Such movements can be constructed to give great precision of measurement. A number of makers employ this principle in their higher grades of instruments.

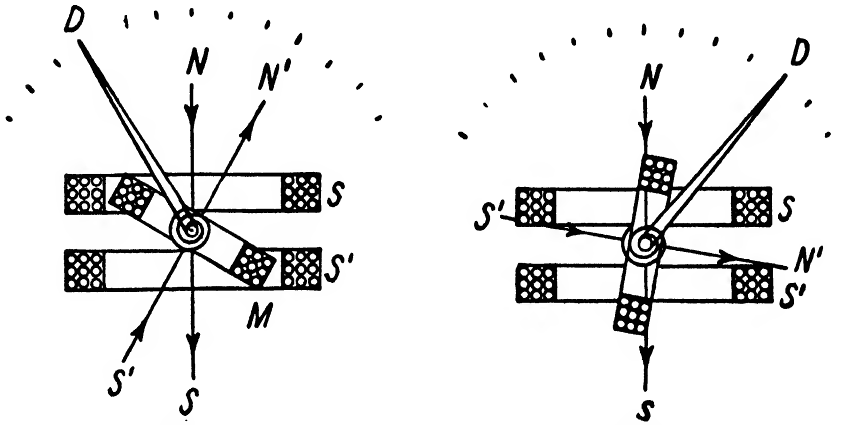


Fig. 4. Fig. 5.

Direct Deflection Electrodynamic Element.

Figures 4 and 5 illustrate the direct-deflection electrodynamic element. A single moving coil works in the field produced by the fixed coils, usually two in number. Since the presence of iron in the movement would usually introduce errors—because of the high inductance of the circuit, and of possible distortions of wave form—it is usual that such movements be "air-cored." In consequence an electrodynamic instrument usually takes from the measured circuit a much greater amount of power than would be required by a permanent-magnet moving-coil instrument of the same measuring range.

Thermal Elements. The thermal-expansion or hot-wire type of element depends upon the expansion of a wire heated by the current to be measured, a small movement of the wire being mechanically multiplied into a relatively large pointer deflection. This type may be used with equal facility on direct and alternating current. The power consumption is almost prohibitive in the hot-wire voltmeter. In the measurement of high-frequency currents, hot-wire instruments are not subject to certain errors which may characterize electromagnetic types.

Electrostatic Elements. The electrostatic type of electrical measuring element has found considerable application as a voltmeter. Its great advantage lies in its low energy consumption: zero on direct current and usually of negligible value on commercial-frequency a.c.

Elements Operable on Alternating Currents Only—The general type of instrument which performs measurement on alternating currents solely by virtue of the fact that these are alternating, is known as the induction type, employing a principle not unlike that of the "split-phase" motor.[1] The current under measurement produces an alternating field in an air-gap wherein lies a rotor or electrically conducting non-magnetic metal. By means of a pole-shading circuit the alternating field is resolved into two out-of-phase components, thus producing a rotating field. The conducting rotor, lying in this field, is constrained to follow the traveling flux, and its torque is opposed by spiral springs. Figure 6 is a diagram of a Westinghouse induction instrument. The induction element has found wide application as a voltmeter, ammeter and wattmeter; and while at present it is giving place to the moving-iron and electrodynamic types in indicating instruments, it practically monopolizes the field in the a-c. watthour meter. Direct current passed through the circuits of an induction instrument produces no effect other than a slight tremor at the instant of being applied and removed.

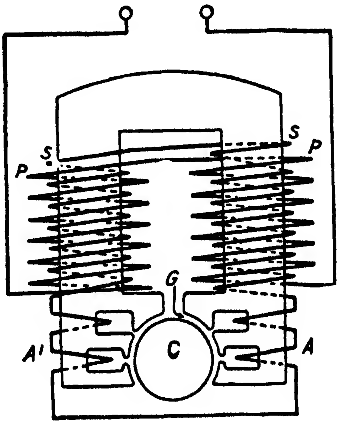


Fig. 6. Diagram of Westinghouse Induction Instrument.

Galvanometers—In laboratory work a galvanometer is usually an instrument in itself. Being designed for utmost sensitivity (10^{-9} amp. is not uncommon) it requires vibrationless mounting. In process measurement and control work, a galvanometer is usually a seldom-seen component of an industrial instrument such as a self-balancing potentiometer or bridge. Being designed and constructed for switchboard service, it is above all a small and rugged device. When a galvanometer is merely employed as the unbalance-detecting element in the industrial-instrument measuring system of which it forms part, it does not "measure" the unknown: its function may be likened to that of a magnifying glass for reading the vernier of a high-grade surveying instrument. However, in the majority of classes and types of industrial electrical instruments, the element frequently referred to as the "galvanometer" is not only a measuring element but *the* measuring element. Actually, it is a milliammeter, a millivoltmeter, a microammeter or a microvoltmeter—*i.e.* a *calibrated* meas-

[1] A single-phase induction motor equipped with an auxiliary winding, displaced in magnetic position from, and connected in parallel with, the main winding.

uring element—most frequently of the permanent-magnet moving-coil type. Note, however, that whereas most measuring elements of this type embodied in ordinary deflection instruments are "side-zero," most of them must be "zero-center" when incorporated in null-method recording or controlling systems. An easily-accessible zeroing knob or screw is provided, but in spite of this provision the galvanometer must be much more stable than a laboratory galvanometer which is under the direct observation of the user. In addition to smallness, ruggedness and stability, industrial-instrument galvanometers must meet the high speed requirements of multiple-point recorders, automatic control systems, etc. These four attributes characterize the galvanometers produced in quantities for well-known makes of industrial potentiometers, telemetering systems, etc. Such galvanometers are far superior to laboratory galvanometers in nearly all properties other than sensitivity. When "galvanometer trouble" is reported by users of elaborate industrial instruments, it generally turns out to be due to faulty incorporation or installation.

Combination Instruments—Only "simple" electrical instruments ("movements" plus essential appurtenances) have been discussed above. There are other types which, though more complex as electrical measuring devices, constitute single elements in industrial instrumentation equipment—as do those discussed above. The most important types are the *Rectifier*, the *Thermocouple* and the *Vacuum-tube* (or *Thermionic*) types.

The *Rectifier type*, as its name implies, consists of a d-c. movement associated with rectifiers. It permits making a-c. measurements with inexpensive moving-iron or permanent-magnet moving-coil d-c. movements. It has been made possible by the commercial development of copper-oxide rectifiers in 1931-34. Though still subject to various errors and troubles, rectifier instruments are fast growing in applications.

The *Vacuum-tube type* utilizes the rectifying and amplifying characteristics of triodes (three-element vacuum tubes). There are five distinct types—five distinct networks—all comprising not only a triode and a milliammeter but various components such as capacitors, resistors, batteries, etc. Self-contained ready-to-use vacuum-tube instruments are a-c. voltmeters primarily designed for communications work and seldom used for chemical process-control work; but the *principle* is extensively used in electrochemical measurements and numerous other applications.

The *Thermocouple type* is a "thermal type" (see page 182) in that it utilizes the heating effect of a current but it is not a simple instrument movement: its principle is the measurement of the temperature of the hot wire by means of another instrument which is essentially a thermoelectric pyrometer. Although the pyrometer part is a millivoltmeter, the instrument as a whole is an ammeter. Since the heating effect varies as the square of the current, the scale law is (roughly) quadratic. The main advantage being minimal frequency error, this type finds important applications in high-frequency work. Numerous styles of open and vacuum thermocouple constructions have been adopted by the various makers.

Potentiometers and Bridges—The industrial applicability of the fundamental electrical elements discussed in the foregoing section is vastly extended by the use of null-method circuits, namely potentiometers and bridges. In brief, these are circuits whereby, instead of converting an electrical effect into a mechanical force and opposing it by a spring, an opposing electrical effect of the same nature is applied, thus bringing the system to *electrical balance.* In the potentiometer, the unknown electromotive force or potential difference is balanced by an emf which is accurately known because it is obtained from a tangible standard of fourth-decimal precision. In the bridge, the unknown resistance is balanced by a resistance which is accurately known because it is itself a tangible standard as trustworthy as a set of precision weights.

Moreover, the condition of electrical balance implies that no current flows in the measured circuit. In industrial work this permits the use of inexpensive copper wiring between elements and control boards; it is essential with various types of electrochemical measurement cells; and it has numerous other practical advantages.

The simple principles of potentiometers and bridges are well known to all technical and scientific men and so need not be discussed further here. When they are used in industrial instruments there are many complications and details which must be taken into account but space limitations do not permit discussion of the many points involved.

RELAY OR "SERVO" SYSTEMS

The proper functioning of many recording, integrating, telemetering and controlling instruments depends upon the employment of relays whereby the measuring element does no work other than to command a servo mechanism. The most important categories of relays in the field of instrumentation are: (1) hydraulic, (2) pneumatic, (3) mechanical, (4) electrical, (5) high-frequency electrical, (6) electronic, (7) photoelectric. Literature on relay systems and servomotors could fill a five-foot shelf; a thick volume could be written on the possibilities of existing combinations; only the sketchiest of notes can be included here.

1. **Hydraulic**—Ample power, positive operation and possibility of locking-in-place of power cylinders are the most obvious characteristics. In general the action is relatively slow, but accurate adjustment of speed is an advantage. On the other hand, jerky action is all too frequent in some cheap systems. Most longitudinal-motion pilot valves consume too much energy to be suitable for actuation by electrical movements and by most other measuring elements. This undesirable erratic drag effect has been minimized in the newer pilots and almost eliminated in the Askania pivoted "jet pipe" relay and in the new (1941) Hagan pilot valve. Prodigious ingenuity is evident in recently invented hydraulic circuits (mostly inspired by those of turbo-generator governors) which permit achieving results close to perfection.

2. **Pneumatic**—Characteristic feature of the usual dead-end and bleed arrangement is a single controlled-air line between pilot and power device, so that the action is unidirectional. In the usual power device a flexible diaphragm is forced in one direction by the compressed-air pressure and in the other by a spring. The characteristic "give" prevents lock-in and, if the controlled valve is imperfectly balanced, droop is inevitable. However, there have appeared secondary pneumatic relay systems known as "regulators," "valve positioners," etc., which provide micrometric lock-in when properly adjusted. Recent devel-

opments in pneumatic circuits comprising a plurality of relays (similar to "cascading" and "feed-back" with electron tubes) have added *stability* and have thus made the pneumatic system capable at last of meeting difficult variable-load requirements.

3. **Mechanical**—Surprisingly few mechanical relay and amplification systems have been utilized by industrial instrument designers. They are found mostly in the integrating and totalizing instruments. The enormous disproportion between the total number of classes and types of escapements, clutches, triggers, torque amplifiers, etc., and the total number in use precludes further discussion here, except to invite the reader's attention to the fact that the proper performance of many instruments employing mercury switches, electric contacts, etc., depends upon the correct functioning of mechanical relays actuated by feeble measuring elements, which in turn operate the electrical devices.

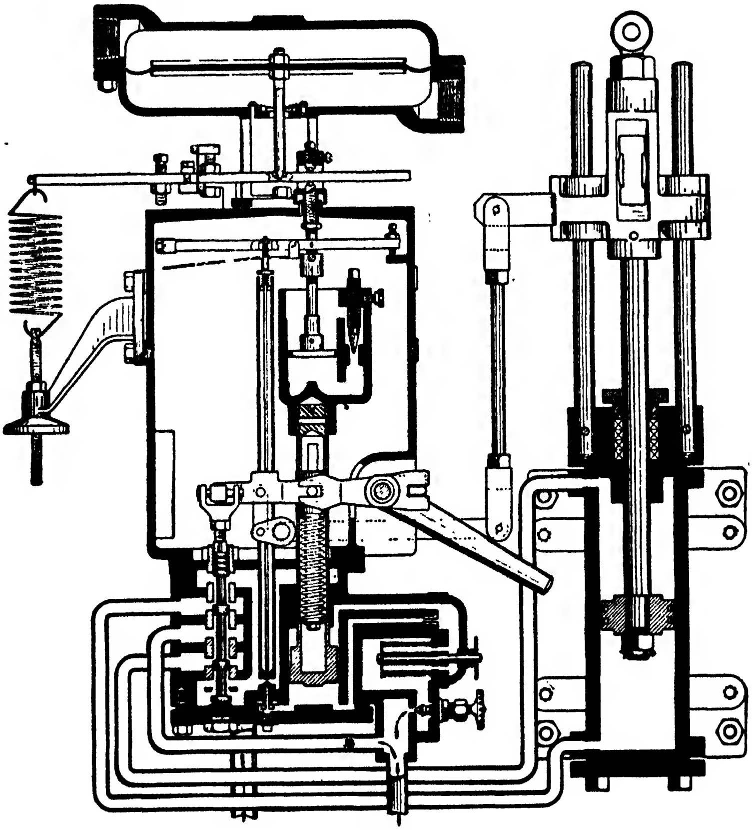


Fig. 7. Smoot Hydraulic Relay.

4. **Electrical**—The great majority of electromagnetic relay systems in industrial instrumentation are "on-and-off" devices whereby circuits are instantaneously opened or closed. The simplest are those wherein contacts are directly attached to the pointers. There are also several types which provide "throt-

tling" modes of control—some step-by-step, others continuously-variable. The simplest arrangement, to have the instrument pointer "wipe" a rheostat, imposes a drag on the measuring system and can only command fractional-horsepower motors. A modification is to have the pointer "wipe" a voltage-dividing resistor (commonly and erroneously called a "potentiometer") which in turn positions a solenoid-and-contactor balancing arrangement commanding a relatively large motor. The effect of a continuous variation or "throttling" is obtained by vibrators and other circuit-interrupting devices (some of which are combination mechanical and electrical relays) whereby the closed-circuit time in each cycle is a function of the position of the pointer. The resulting mode of control is applicable only to processes with adequate energy storage or "flywheel effect." Therefore this equivalent of throttling is chiefly used for the control of electric heat.

Air Valves

DIRECT-ACTING

Allows compressed air to flow to the diaphragm-motor when the transmitting lever moves away from the pin. May be embodied in all types of controllers.

REVERSE-ACTING

Allows compressed air to flow to the diaphragm-motor when the transmitting lever bears against the pin. (Is not embodied in mercury system temperature controllers.)

Diaphragm-Motor Valves

DIRECT-ACTING

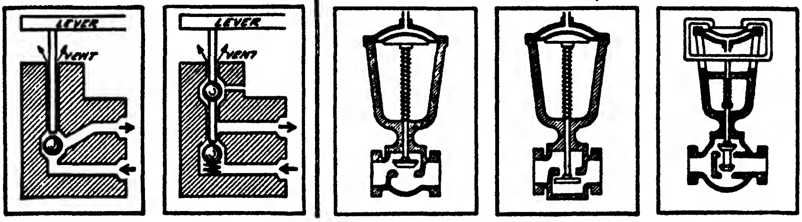
Closes on admission of compressed air to diaphragm top. When air is released, valve opens, as steam pressure is under the disc, and spring assists in opening.

REVERSE-ACTING

Opens on admission of air to top. When air is released, disc rises up against seat and closes valve. Spring assists in closing. When air fails, valve closes—a safety feature.

WITH REVERSE-ACTING TOPS

The air is below the diaphragm, and the saucer is located above it. Admission of compressed air opens the valve. Should air fail, valve will close.



Characteristics of Combinations

Application	Type of Controller	Type of DMV	When Temperature or Pressure		Forms of DMV's	Valve Size Limit
			Rises Above Setting Point	Falls Below Setting Point		
Heating (or Pressure Reduction)	Direct Acting	Direct Acting	DMV Closes Throttling Action	DMV Opens Throttling Action	Single and Double Seated	12"
	Reverse Acting	Reverse Acting	DMV Closes Throttling Action*	DMV Opens Throttling Action*	Single and Double Seated	12"
	Reverse Acting	With Reverse Acting Top	DMV Closes Throttling Action	DMV Opens Throttling Action	Double Seated Only	4"
Cooling (or Excess Pressure Relief)	Reverse Acting	Direct Acting	DMV Opens Throttling Action	DMV Closes Throttling Action	Single and Double Seated ·	12"
	Direct Acting	Reverse Acting	DMV Opens Throttling Action*	DMV Closes Throttling Action*	Single and Double Seated	12"
	Direct Acting	With Reverse Acting Top	DMV Opens Throttling Action	DMV Closes Throttling Action	Double Seated Only	4"

(*) Except single-seated reverse-acting valves over 2" which will not throttle.
By double-seated valve is meant a balanced valve. By single-seated valve is meant a globe valve type not balanced or not gate type. Single-seated balanced valves are available but of special construction.

FIG. 8. Diagrams of Tagliabue Pneumatic Instruments.

5. **High-frequency Electrical**—This designation has been adopted to convey unmistakably the idea that this class of relay systems utilizes the properties of a-c. networks. Since most a-c. phenomena manifest themselves at low (commercial) frequencies, the designation "a-c. relays" would be correct but it already denotes a class of devices different from the systems here considered.

The outstanding characteristic of these relays is the possibility of eliminating drag by doing away with contacts and pilot valves. In some systems the pointer or equivalent element serves as one plate of a variable capacitator, in others it serves as the control element in an inductive coupling, the mechanical reaction in either case being negligible. Aside from these pointer-displacement systems there are others in which the relay action is effected without mechanical motion. These latter, of course, can only be used in conjunction with "static" measuring systems in which the measured physical condition, chemical property, etc., is translated into an exactly proportional electrical magnitude.

6. **Electronic**—In this newest class of instrumentation relay systems the relay proper is an electron tube, directly actuated by or fed from the measuring element or system. Although relatively few of the hundreds of commercial types of electron tubes are suitable as prime relays, other types are employed in the numerous circuits which have been developed to take full advantage of the general characteristics of electronic relays. First among these general characteristics is suitability for actuation by static measuring elements. Conversely, no ordinary pointer-and-scale type of measuring element can be equipped with an electronic relay and no ordinary type of electron tube can serve as a relay in conjunction with a mechanical-displacement type of measuring element.[2] Second outstanding general characteristic is enormous amplification: up to 1500× in each stage. Third general characteristic is instantaneity. Other general characteristics (to which there are exceptions) are: limited life, gradual or sudden alteration of tube constants without outward sign, fragility, low cost of "spares," ease of replacement, and relative instability where the "signal" from the measuring element is of the order of millivolts d.c. Electron tubes differ from all other relays in that while the "constants" of a tube are mostly inherent and are intended to be unaffected by external factors, its operating characteristics depend on external factors such as character of signal, whether the load is purely resistive, inductive, capacitive or combination, etc. Summing up, we may say that the single type most suitable for relay service as understood here, may be described as follows: high vacuum, thermionic-emission or heated cathode, amplifier tube with one or more electrostatic control electrodes. So numerous are the built-in means of control (including "inversion" schemes

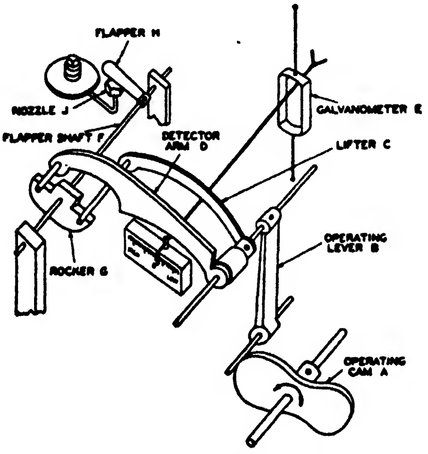


Fig. 9. Foxboro Mechanical Relay.

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[2] **Phototubes are not electronic relays: even when the condition to be measured is illumination, a phototube cannot be the relay because it is the measuring element. The same is true of the "ionization gauge" triode: it is the primary vacuum-measuring element in itself. The same is true of a mercury-vapor-type grid-controlled rectifier when used as the temperature-responsive element in a thermostat.**

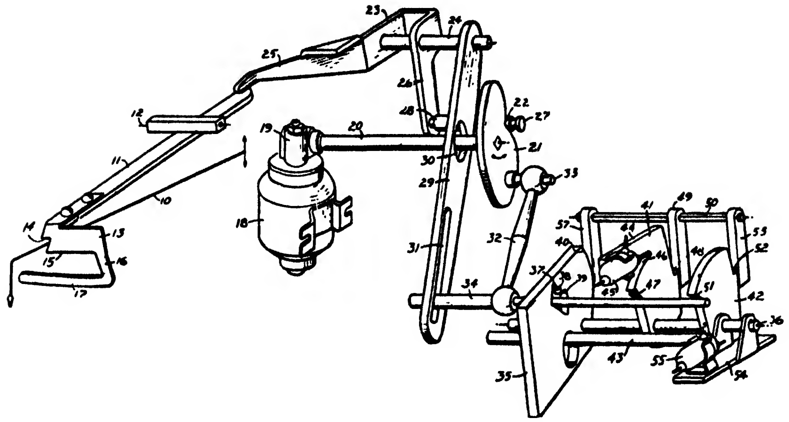

FIG. 10. Republic Flow Meters Co. Mechanical Relay Electrically Driven.

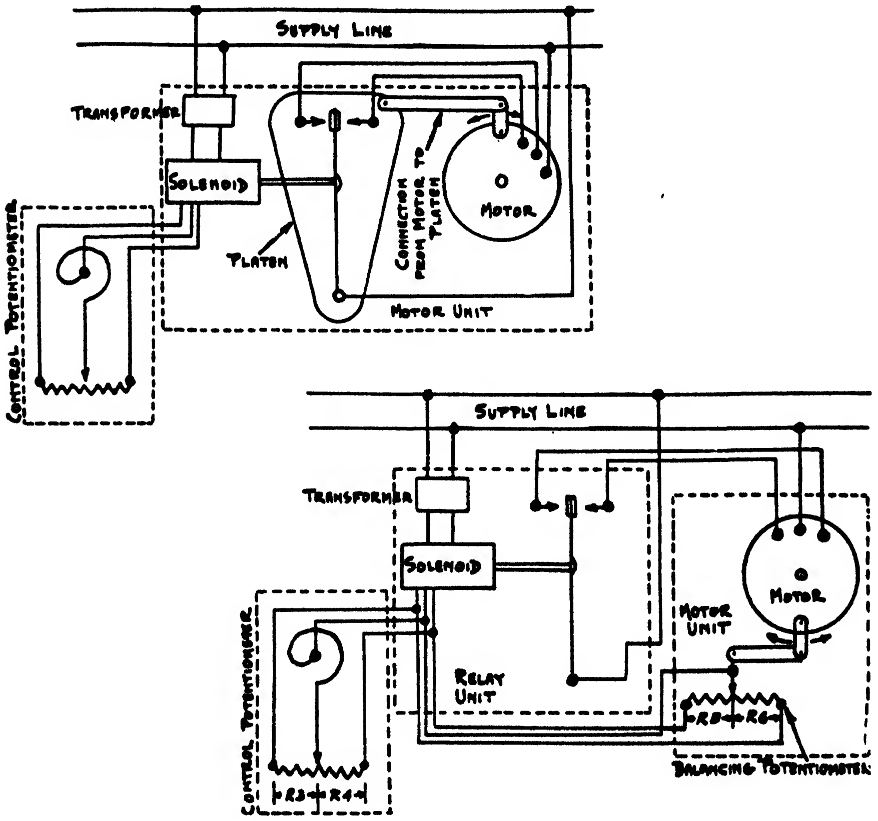

FIG. 11. Minneapolis-Honeywell Regulator Co. Electrical Relay Systems.

with grid anodes, etc., specially designed for measurement work) and the external methods of control ("hook-ups") that further discussion cannot be attempted here.

7. **Photoelectric**—This class of relays comprises both phototubes and photocells. Outside the field of instrumentation the former are considered "electron tubes" and in nearly all texts they are lumped together with the electronic relays discussed in the foregoing paragraph, while photocells are excluded. For our purpose the only criterion is that electronic relays respond to purely electrical effects and have purely electrical outputs; whereas photoelectric relays are all those which respond to light and have electrical outputs. There are three classes of such devices: (1) "selenium" or photoresistive tubes and cells—originally the only ones but seldom used for instrument work today; (2) photoemissive, comprising various forms of vacuum and gas-filled glass tubes with various forms of cathodes coated with various alkali-metal materials; (3) photovoltaic or blocking-layer, theoretically comprising all types but in practice excluding the Becquerel liquid electrolytic cells and made up only of the dry disk form cells—chiefly cuprous oxide on copper but lately including selenium-on-iron and other new developments. All are widely used as measuring elements but this is not the function considered here. The outstanding characteristics of all phototubes and photcells, *used as relays*, are (1) total absence of drag on the measuring element; and (2) practically instantaneous response—the lag of the "selenium" and blocking-layer classes being negligible in relay service. Other characteristics differ widely with the classes and types. There is no such thing as a phototube or photocell with perfectly and permanently linear characteristic of electrical output to intensity of illumination: all suffer to some extent from fatigue, temperature coefficient, etc., but these effects are immaterial in the simple trigger relay applications. Therefore, in applica-

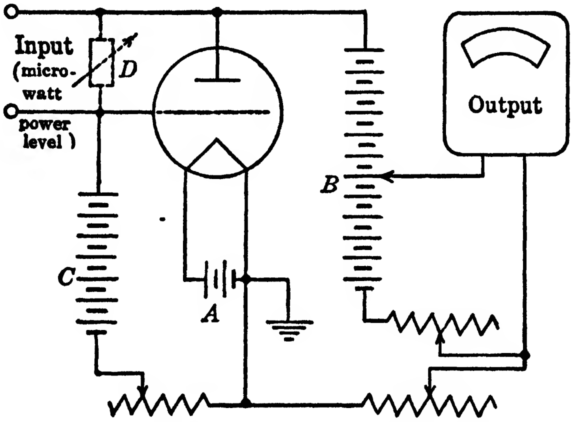

Fig. 12. Electronic relay—single-stage "electrometer type," amplifying type, output serving to actuate a switchboard instrument.

Generalized elementary diagram. Nature of device D depends on source and nature of input signal: if source is of practically infinite internal resistance and signal a d-c. potential, D should be a resistor of the order of megohms; if signal is a.c. or "chopped" d.c., D should be a capacitor.

tions requiring proportionality, phototubes or photocells are preferably used in pairs and the deflection of the measuring element is a function of the *ratio* of the light falling on each.

This brief treatment of instrumentation does not pretend to be sufficiently complete to serve as a guide for the selection, installation and operation of instruments. It merely indicates the general principles upon which they operate and, to a certain extent, what they will or will not do. To obtain more complete information in this field it will be necessary to go to books which deal exclusively with the subject, to technical periodicals and to manufacturers' descriptive catalogs.

The brevity of this chapter is not to be taken as any indication of the importance of instruments in chemical industry. Increasingly, industrial chemical processes are made or broken by the quality of instrumentation and automatic control. Sometimes instrument cost represents as much as half of the total plant investment. This gives a measure of their importance in the eyes of the practical, practicing directors of chemical industry.

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CHAPTER 6

WATER FOR MUNICIPAL AND INDUSTRIAL USE

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INTRODUCTION

The subject of water supply is of twofold interest to the industrial chemist because the business of supplying water involves chemical engineering problems and because water is a fundamental requirement in many chemical operations. Among the many problems present in this field, the chemical engineer is primarily interested in the nature of the sources, examination and purification of natural waters.

The importance of a dependable water supply was recognized in very ancient times. The digging of wells dates back to early Chinese and Egyptian history and the aqueducts of the ancient Romans are numbered today among their remarkable engineering achievements. Like every other mark of civilization, the importance of dependable water supply was lost sight of in the Middle Ages, and it was not again definitely recognized until the eighteenth century, when London and Paris began to adopt the principle of a water supply for individual houses. In these early house supplies, however, the water, without purification, was turned on for only a short period each day and such intermittent service was not entirely superseded until almost the end of the nineteenth century. There has been an enormous expansion since the advent of cast-iron pipe and power pumps, and analytical purity control, until today water of established purity is almost universally supplied and utilized.

The largest water requirement is that for municipal use, but the standards of purity for this purpose are sometimes quite different from those demanded for industrial and commercial usage. For manufacturing purposes the quality of water may be so important as to be the controlling factor in the location of an industry. Knowledge of the character of available water supplies, as well as knowledge of the effects of impurities in water on industrial processes, is therefore essential to a wise choice of plant location.

SOURCES AND NATURE OF WATER SUPPLY

Rainfall is the ultimate source of all fresh waters, though water supply is usually directly acquired, either from surface waters, such as lakes and rivers, or from ground waters, such as springs and wells.

There will be, of course, seasonal variations in the rainfall which will be reflected in the quantity and quality of the water supply. The swollen turbid floods of springtime and the low water of late autumn, the variations of rainy and dry seasons, are well known. Thus, for example, in Philadelphia where the annual rainfall is about 40 inches there is scarcely any seasonal variation, while in San Francisco where the annual rainfall is about 20 inches, less than 5 per cent of this falls in the four summer months, June to September, while nearly 45 per cent falls in the two winter months December to January. Variations for typical cities are shown in the accompanying Table 1. In addition, there will be annual variations, that is, wet and dry years. The amount of this variation may run from 20 per cent or less on the U. S. Atlantic Coast to 75 per cent or more in the Western States. The following Table 2 shows the average annual precipitation for the United States as a whole since 1870 and reveals 1889 as wettest year, 36.9 per cent wetter than average, 1935 as driest year, 23.8 per cent drier than average, in that period. The per cent of the total rainfall which becomes available in the streams, the so-called run-off, is further dependent on the nature and porosity of the soil, the density of vegetation, etc. For example, the run-off in the Northeastern United States is about 60 per cent of total rainfall, so that a survey of water supply possibilities in a given region will involve the study of all these factors.[1]

TABLE 1—MEAN SEASONAL RAINFALL IN REPRESENTATIVE STATES

States	*Spring Rainfall* *Inches*	*Summer Rainfall* *Inches*	*Autumn Rainfall* *Inches*	*Winter Rainfall* *Inches*	*Annual Rainfall* *Inches*
Massachusetts	11.6	11.4	11.9	11.7	46.6
New York	8.5	10.4	9.7	7.9	36.5
Pennsylvania	10.3	12.7	10.0	9.5	42.5
Virginia	10.9	12.5	9.5	9.7	42.6
South Carolina	9.8	16.2	9.7	9.7	45.4
Alabama	14.9	13.8	10.0	14.9	53.6
Louisiana	13.7	15.0	10.8	14.4	53.9
Kentucky	12.4	12.5	9.7	11.8	46.4
Illinois	10.2	11.2	9.0	7.7	38.1
Minnesota	6.5	10.8	5.8	3.1	26.2
Nebraska	8.9	10.9	4.9	2.2	26.9
Colorado	4.2	5.5	2.8	2.3	14.8
Montana	4.2	4.9	2.6	2.3	14.0
California	6.2	0.3	3.5	11.9	21.9
Average	9.2	10.3	8.3	8.6	36.3

Compiled from data in Yearbook of U. S. Dept. of Agriculture, 1932, pp. 920-922. Covering the years 1881-1930.

NATURAL WATER IMPURITIES

All natural fresh waters contain impurities and the nature and quantity of these impurities are dependent on the conditions under which the waters have accumulated. The value of a water supply is, therefore, closely associated with the nature of its source.

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[1] For detailed information on the quantity and character of waters in the United States the reader is referred to U. S. Geological Survey Water Supply Papers Nos. 489, 496 and 658.

The impurities usually found in natural waters may be classified as suspended and dissolved. The former includes microscopic and bacteriological impurities. Suspended impurities produce turbidity and may range from nil in a clear spring water to the dense mud of the lower Missouri River. Dissolved impurities usually consist of the carbonates, bicarbonates, chlorides, and sulfates of calcium, magnesium, and alkalies, and may range from a few parts per million in snow water up to several thousand parts per million in mineral springs. Other soluble impurities such as silica, iron, alumina, nitrate, etc., may be present to the extent of a few parts per million. Microscopic impurities include the varieties of plant and animal life above bacterial and may range in quantity up to such concentrations that they impart strong turbidity, color, taste, or odor to the water. Bacteriological contamination may include yeasts and molds as well as bacteria, and is usually estimated both in terms of total number of all species and number of gas-forming organisms. The total number may range from a few per cubic centimeter in a deep-well water to thousands per cubic centimeter in a surface water. Gas-forming bacteria may range from none in a mountain stream to hundreds or even thousands per cubic centimeter in the polluted waters of a densely populated region.

TABLE 2—AVERAGE UNITED STATES ANNUAL PRECIPITATION 1871-1938

Year	*Precipitation Inches*	*Year*	*Precipitation Inches*	*Year*	*Precipitation Inches*
1871	48.80	1896	37.99	1921	34.38
1872	45.78	1897	44.27	1922	43.38
1873	39.98	1898	45.12	1923	36.72
1874	39.84	1899	42.06	1924	37.72
1875	45.19	1900	41.78	1925	36.52
1876	47.40	1901	47.06	1926	49.68
1877	40.94	1902	47.07	1927	49.90
1878	46.66	1903	48.60	1928	40.73
1879	36.21	1904	41.57	1929	39.13
1880	37.34	1905	44.48	1930	35.33
1881	40.40	1906	41.82	1931	35.50
1882	46.61	1907	45.28	1932	38.85
1883	38.83	1908	41.43	1933	49.68
1884	55.34	1909	41.55	1934	44.96
1885	42.12	1910	35.98	*1935*	*32.64*
1886	46.73	1911	40.34	1936	46.33
1887	46.63	1912	38.50	1937	48.13
1888	52.95	1913	44.39	1938	46.40
1889	*58.68*	1914	33.50		
1890	52.30	1915	40.83		
1891	41.44	1916	33.17		
1892	38.90	1917	39.28		
1893	53.01	1918	33.59		
1894	44.17	1919	48.38		
1895	35.73	1920	48.81		

U. S. Dept. of Agriculture, Weather Bureau (Pamphlet), "Annual Meteorological Summary with Comparative Data," 1938, compiled under direction of James H. Kimball, New York, N. Y. (1938).

Rain Water—Rain, the purest of natural waters, may collect finely powdered mineral matter, particles of plants, ammonia, carbon dioxide, oxygen, nitrogen, and other substances gathered in its fall through the atmosphere. On reaching the earth, rain flows into streams as surface run-off, passes into the air as vapor, or sinks into the ground, a storage reservoir from which it eventually emerges as vapor or surface water or is recovered as ground water.

Surface Waters—The term "surface water" is applied to the natural water in streams, ponds, and lakes, although it is understood that such waters may have percolated more or less through the soil in their course to the open streams. Actual surface drainage is the chief contributor of turbidity to streams, while the percolated water is responsible for a major part of the dissolved mineral impurities. Whether passing over the surface or slowly percolating underground, water takes into solution a part of the materials with which it comes in contact. Impurities derived from the air assist in the solution of rock-forming minerals, while all the dissolved materials exert an influence one upon another. The chemical constitution and physical conditions of an area are therefore reflected by the water it furnishes.

Amount and intensity of rainfall, assisted by surface slope and permeability of soil, play an important role in the quality of water. Other things being equal, least mineral matter is found in waters from regions of highest rainfall. In periods of drought, ground water is the chief source of stream flow and in consequence the stream waters are thus concentrated. A gentle rain will increase the ground water and cause it to feed the streams more generously but will not contribute appreciably to stream flow by means of surface run-off. A hard rain, on the contrary, may contribute comparatively little to ground water but will wash much dirt into streams, increase their loads of suspended matter, and dilute their dissolved mineral impurities. The amount and character of impurities in surface water, therefore, depend on numerous conditions and are derived from many different sources.

Ground Waters—The waters obtained from springs and wells in a given locality may be very different from the local surface waters. Most well and spring waters indicate the nature of a very local geologic area, while running streams reveal the conditions of their drainage areas and thus provide an approximate average index of the geology of a much larger territory. Stream waters are usually the lower in dissolved mineral content but vary greatly with change of season in dissolved impurities, turbidity, and chemical character. Ground waters are more nearly constant in composition but are likely to contain deleterious gases, relatively high concentration of mineral constituents, and are the more pronounced in chemical type.

Ground waters are normally the more concentrated the deeper the horizon from which they are drawn. The older crystalline rocks afford waters of low concentration free from permanent hardness, though temporary hardness and relatively high content of silica may be expected. Such waters are prevalent in the upper Mississippi River basin, in the region from the Appalachian Mountains to the Atlantic coast, from New England to the Gulf of Mexico, and in relatively small areas in various sections of the United States. Waters from basalts and rhyolites, such as are found in many parts of the Rocky Mountain and Pacific

Coast States, are likely to be somewhat more concentrated and may carry much sulfate. Sedimentary rocks, particularly marine sediments, such as are found throughout the greater part of the Mississippi Valley, afford waters of still greater concentration. Waters from limestones are very hard and those from magnesia limestones and dolomites carry both scale-forming and corrosive ingredients.

Sandstones differ greatly in content of soluble constituents and in quality of waters, and this is true also of shales. The best and worst of industrial waters may come from shales of widely differing character. Many sandstones and shales afford waters of high permanent hardness. These rocks, like the limestones, cover great areas, and once the character of the water from any particular stratum is determined, the general characteristics of a water from the same stratum many miles distant can be forecast with a fair degree of accuracy. In general, ground waters are not as desirable for industrial purposes, but may be as satisfactory for sanitary use as surface waters. This may be inferred from their tendency to higher mineral content and lower turbidity and organic content.

MODERN REQUIREMENTS OF WATER SUPPLY

The quantity of water required daily in a district is usually stated in terms of per capita consumption, though the figure includes domestic, commercial, and public use. An actual domestic demand of forty gallons per capita is considered average. Commercial use varies greatly according to type of community, but, all told, represents a consumption comparable with domestic use. Public use and leakage, together, represent also a similar quantity. Thus the total water requirements for all purposes of the average district will be somewhat above 100 gallons per day on the per capita basis. Exceptions are found in such industrial centers as Buffalo, 325; Pittsburgh, 225; Detroit and Chicago, 200 gallons per day per capita.

These figures do not include the consumption of industrial plants with private water works. In many of these, the principal consumption is for condensing purposes, and, as an illustration of the quantities which may be involved, the daily use and re-use of water from the Mahoning River at and below Youngstown, Ohio, is several times the entire daily flow of the river. Eleven thousand communities in the United States and Canada have public water supply and the investment in equipment for collecting, distributing and purifying municipal supplies is increasing at the rate of $125,000,000 per year.

The purity requirements of water supply vary according to the specific industries served and these may, therefore, be considered individually.

Requirements for Municipal Supply—The quality requirements of municipal water supply are concerned primarily with physical and biological standards and to a minor extent with chemical composition. The standards established by the U. S. Treasury Department and published June 20, 1925, are usually accepted by public water works.

According to these specifications such water supply shall be derived from a source free and protected from pollution and the mean density of bacteria of the B. coli type shall not exceed about one per hundred cubic centimeters. It shall be clear, colorless, odorless, and pleasant to the taste and shall not contain an excessive amount of soluble substances or any chemical employed in treatment.

The upper limit expressed in parts per million for certain soluble substances is: iron, 0.4 p.p.m.; magnesium, 100 p.p.m.; sulfate, 250 p.p.m.; chloride, 250 p.p.m.; and total solids, 1000 p.p.m. Most municipal water supplies come much below these limits[2] and a water just within the limits would be highly unsuited to most industrial purposes.

Many municipalities, to encourage the establishment of industries within their territory, provide a water supply which will meet not only sanitary standards, but which is also suited to industrial requirements. To accomplish this, they may spare no expense to bring high-grade waters from a considerable distance, and often install extensive purification plants for the removal of deleterious impurities.

Water for Irrigation—On first thought, it might seem that water for irrigation need not be different from ordinary river water, but it is readily seen that irrigating water for the most part is eventually evaporated from the soil over which it is spread and therefore leaves all its soluble impurities behind. These will gradually concentrate in the surface of the ground and may eventually become very detrimental to plant growth. Land would probably be injured by the best of natural waters if irrigated with them for too long a period of time without natural or artificial drainage. High alkali content is particularly detrimental and the value of a water for irrigating purposes is roughly established by its content of alkaline substances. The higher the alkalinity the greater is the portion of the water which will have to be drained away from the irrigated area to keep it flushed out. Hence the value is decreased not only because of the poorer quality but because of the larger quantity required.

Water in the Textile Industry—The textile fibers, including wool, silk, and cotton, are prepared for fabrication by scouring processes which involve the use of quantities of water.[3] The standards of purity required are high in all cases but vary with the specific operations.

Wool Scouring—In wool scouring, all fresh water is added in the third or final scouring tank from which the wool emerges in its finished condition. Impurities in the water that will cling to the fiber, therefore, are obviously out of place and will have the same deleterious effects in subsequent processes as imperfect scouring. Suspended impurities are generally undesirable, organic matter being especially deleterious. Therefore, waters polluted by sewage or organic industrial wastes and turbid waters are always purified before use in scouring-tanks.

A second, and even more important class of impurities, consists of those substances which unite with soaps used in scouring to form insoluble soaps. These substances, iron, aluminum, calcium, and magnesium, destroy their equivalent values of soap for detergent purposes, thereby making necessary the use of an excessive amount of soap.[4] In addition, the insoluble soaps stick closely to the fiber and make efficient scouring very difficult. On this account, they are more detrimental to the process than inorganic suspended matter composed largely of colloidal particles of clay. Priestman[5] states that water containing 30 English degrees of hardness (428 parts per million of calcium carbonate) cannot be used

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[2] For discussion of water quality standards see Streeter, H. W., J. Am. Water Works Assoc. *31*, 1479 (1939), and Baylis, J. R., ibid. *32*, 1753 (1940).

[3] See also Chapter 29.

[4] For discussion of use of detergents, see Chapter 42.

[5] Priestman, H., "Principles of Wool Combing," George Bell & Sons, London (1904).

for satisfactory washing and adopts 5° of hardness (71 parts per million of calcium carbonate) as the limit of "hardening" constituents for a satisfactory water supply.

In scouring by the two-stage process of steeping and scouring,[3] the importance of pure water is even greater, for, in addition to the effect of hardness in the scouring operation, the recovery of potash from the steep water will be rendered somewhat more expensive and the purity of the product will be decreased by the saline constituents of the water. In this case all mineral impurities, not merely the hardening constituents, have a deleterious effect.

In scouring by volatile solvents and subsequent washing, since no soap is used, purity of water is a minor consideration. Suspended matter, of course, is undesirable. If the wash water is utilized for the recovery of potash, all dissolved impurities will assume importance, inasmuch as some will cause scale in the evaporators and all will decrease the purity of the potash produced. Each 100 parts per million of mineral solids in the water will reduce the purity of the potash by approximately 1 per cent. If the wool is scoured by one of the newer detergents such as the sulfonated alcohol products like "Igepon,"[6] then the hardness in the water will be of less consequence. This is due to the fact that the calcium and magnesium compounds of these detergents are soluble, hence do not cause a loss of detergent power and more particularly, do not precipitate on, and foul the surface of the wool.

Water used for rinsing the wool after scouring may amount to as much as 100 gallons for each pound of wool scoured. This water should be free from suspended matter, but otherwise requires no special qualities.

Silk Industry Uses—In the silk industry, pure waters are required, as in wool scouring, to conserve soap and prevent contamination from sticky precipitates.

In the first stage of silk manufacture, the raw silk is soaked in a strong solution of soap containing neat's foot oil. This process is necessary to give the silk sufficient softness and pliability for the winding operation. With waters containing lime and magnesium in large amounts, the soap forms a characteristic curdy precipitate which mats the fibers and causes considerable difficulty in winding the silk. Furthermore, the precipitate clings to the fibers, forming soap specks which later harden the silk at these points.

The next operation, that of boiling off,[3] requires the use of greater quantities of both soap and water. The deleterious results of unsuitable water here are, therefore, intensified. Where lime spots form, the silk may become discolored and the fiber will crack. Weighting is largely affected by the lime and magnesium content of the water used in previous operations. Lime spots prevent the absorption of the tin solution at such points, since the fiber is there covered by the sticky lime precipitate. The result is lack of uniformity in weighting and "hungry spots" which later in the dyeing operation produce uneven coloring of the fabric. Brighter colors are said to be produced with soft waters, using less dye, than with other waters containing large amounts of the alkali-earth elements.

Cotton Industry Uses—The cotton industry has long recognized the value of soft water in its operations. The boiling-off requires the use of resin soap in large amounts, which soap, like others, is wastefully consumed by calcium and

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[6] See Chapter 42.

magnesium in the water. The precipitates formed are resinates of calcium and magnesium, which are just as troublesome in later operations as the corresponding oleates and stearates. Spots, difficult to wash out, dye, and bleach, are formed and a uniform white, so essential in this industry, is almost impossible to obtain. It is characteristic of silks and cottons produced by plants using soft water that the fabric has a softer "feel," not at all like the harsh "feel" of fabrics produced with waters containing large amounts of the hardening constituents. In the manufacture of textiles, therefore, the necessity for a clear, colorless water containing as little calcium and magnesium as possible is obvious unless the newer detergents are used.

Rayon Industries—In the rayon industry as in the case of natural fibers the water must be of high purity to give best results. Water must be soft[7] because lime and magnesium salts which are responsible for hardness of water also cause hardness of finish on rayon and interfere with level dyeing. Traces of iron in the water may be highly detrimental as evidenced in a rayon plant operating on the Niagara River. In this plant splotchy discolorations were noted in the product and after much effort, were finally traced to the presence of less than 0.5 p.p.m. of iron in the wash water. When this was removed by suitable treatment (see iron removal) the difficulty cleared up.

Water for Dyeing and Bleaching—Involving, as it does, the use of such small amounts of chemicals and large amounts of water to produce delicate coloring effects, the dyeing of fabrics often presents chemical problems of considerable difficulty.[8] The solution of these problems often hinges on the proper choice or treatment of water used in the process. A water containing large amounts of calcium is unsuitable and even ruinous for use in dyeing with aniline colors, but is essential to the successful use of logwood or weld, dyed on a mordant of iron or aluminum.

Calcium and magnesium act very much alike in dyeing. Some of the effects of these constituents are as follows: Heavy tarlike precipitates form when such aniline colors as methyl violet, malachite green, magenta, and safranine are dissolved in waters high in calcium and magnesium. This tarlike precipitate sticks to the fiber and results in uneven dyeing, poor shades, and that annoying defect of "rubbing off." Magenta and safranine are peculiarly susceptible to the influence of these constituents, the effect being noticeable in changes in both color and intensity of the coloring material. Color is wasted and flat shades are produced in dyeing with Turkey red or cochineal scarlet. On the other hand, in dyeing with alizarin it is necessary to have calcium carbonate present to cause complete saturation of the mordants, but when calcium and bicarbonate radicals are present, carbonic acid is freed, calcium carbonate is precipitated by the heat, and the bath takes a violet color due to the formation of a compound of calcium and alizarin. If the solution is boiled, the lime lake deposits as a violet powder, and the bath cannot be used. Thus it can be seen that calcium may be helpful or detrimental to dyeing according to circumstances, but as a rule, calcium and magnesium salts result in uneven dyeing, fading colors, spotted effects, off-shades, and a waste of color.

Iron is a very objectionable impurity. Dull and flat colors are frequently

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[7] Rayon Handbook, first edition, p. 117.

[8] See Chapter 29.

caused by this constituent, especially when dyeing on a mordant. If a water contains iron in any appreciable amounts, it is practically useless for dyeing or printing with alizarin or for any of the coal-tar colors that are fixed on a tannin mordant. Also in bleaching, iron is a troublesome constituent. The iron is oxidized by the bleach solutions, causing yellow, brown, or muddy white effects. This difficulty can be partially remedied by acid treatment, but there is then danger of injuring the fabric. Laundries have much the same difficulty with ferruginous waters. It is therefore evident that a water suitable for dyeing and bleaching should be free from suspended matter, low in its content of iron, and as soft as possible.

Water in Paper Making—If one considers that from 10,000 to 400,000 gallons of water are used to produce only one ton of finished paper,[9] it can readily be understood that the quality of this water, especially for the finer products, is a matter of some importance. With the coarser grades, such as brown wrapping paper, the composition of the water does not figure so prominently.

While the ordinary constituents of a water which contains permanent and temporary hardness cause little trouble in preparing the pulp, their effect in sizing is decidedly harmful. One type of sizing consists in precipitating, usually with alum, the resin from a solution of a resin soap. The aluminum resinate thus formed is precipitated on the fibers. The well-known reactions between lime and a soap here take place if the water is of a calcareous nature. Carbonic acid decomposes the resin soap, forming sodium bicarbonate and, if calcium is present in appreciable amounts, calcium resinate. This compound has a more granular consistency than the corresponding aluminum compound, does not adhere to the fibers as well, and hence is entirely unsuited for sizing purposes. Alkaline waters give trouble through the formation of double salts with alum causing incomplete or improper precipitation of the aluminum resinate. The difficulty here may be overcome, of course, by the previous treatment of the water with alum, but unless this is a part of a purifying system to which careful attention is paid, large amounts of alum are wasted with but partial prevention of the trouble and variable results.

Turbid waters, or waters carrying suspended matter, are injurious to the product. Such particles resist the action of bleach and cause dark specks and spots in the finished paper, particularly noticeable in white and light shades of fine writing and art papers. Vegetable coloring matter is productive either of streaks or of a dull shade imparted to papers that should be white. Acid waters are among the most annoying offenders. They not only give trouble with the size, decompose the colors, and produce streaks in the papers, but they also attack the expensive wire screens and dryer-felt of the machine.

In making white or light shades of paper, ferruginous waters are out of the question unless the iron is removed. Alkali precipitates ferric hydroxide, which gives the pulp a brown color. During sizing the iron also gives trouble, and rust spots in the finished paper are a common result of the use of water containing iron.

Water in Tanning—Tanning is an industry in which the quality of the water plays an important part.[10] The large volumes of water used both in the unhair-

[9] See also Chapter 37.
[10] See Chapter 45.

ing and in the tan pit make necessary the careful selection or purification of the water supply. Unhairing consists in loosening the roots of the hair by treatment of the hides with quicklime. If the water used in this process contains bicarbonates or free carbonic acid there results a precipitation of calcium carbonate in the dermic tissues. This precipitate naturally interferes with the absorption, by the cells of the hide, of the tannin which is intended to convert the skin into the insoluble material, leather. In the tan pits, calcium and magnesium react with the tannin, destroying its usefulness. A considerable amount of an expensive chemical is thus wasted, and, according to one authority, the secondary products formed impart to the leather a reddish-brown color which lowers the market value of the finished product. One way of obviating this difficulty is to treat the water with a free mineral acid, preferably sulfuric. The acid seems to aid in swelling the hides and if used at the proper concentration for a period of time not too great, no rotting of the hides takes place. Chlorides are harmful to the proper swelling operation since they do not unite with the hide and even prevent the proper action of the acids, but sulfates of calcium and magnesium, preferably the latter, are desirable. In their presence plumping is more readily effected, the finished leather has a finer and more compact grain, and the cut surfaces are cleaner and more shiny.

Organic matter should be entirely absent from water used in tanneries, since one of the prime requisites of the finished product is that it must not decay. Organic matter tends to cause decay or "leather rot," hence its removal becomes a matter of necessity rather than choice.

Iron is objectionable in the water supply of tanneries, since the same reactions which are used in making one kind of black ink take place between the iron of the water and the tannin with which the hides are treated. In both cases, ferrous iron is oxidized by the air to ferric, which then reacts to form black tannate of iron. Such coloration is, of course, ruinous to any but black leathers. Water for tanneries should therefore be clear and low in iron, hardness and chlorides though calcium and magnesium sulfates are harmless for certain of the operations.

Other Chemical Industries—There are many other chemical industries of importance which depend to some extent on the quality of their water supply for successful maintenance. The manufacture of filter paper is a specialized industry in which the final ash content of the finished paper must be as low as possible. Hence the water must be of low total solid content in addition to the requirements necessary for ordinary paper manufacture.

Ice manufacturing is an industry in which, until recently, the necessity for pure water was so highly regarded as to warrant the expense of distillation in order to remove all soluble impurities. This industry differs from some others because any impurities, no matter how soluble, are frozen out of the water, continually concentrating in the unfrozen core of the cake until they pass the saturation point and are precipitated as cloudy solids in the core at the center of the cake. Present-day manufacturers often avoid the expense of distillation by withdrawing the concentrated water solution in the core before precipitation starts, and replacing with fresh water once or twice, thereby reducing the cloudy core to a minimum; but, in any case, the quality of the ice is largely commensurate with the purity of the raw water.

The brewing industry is one requiring large amounts of water both in the malting and fermenting process and it is recognized that mineral salts may be very injurious in both of these processes. In the case of malting, a low concentration of sulfate is not altogether undesirable, but, if carbonates are present in either this or the later stages of manufacture, the final product will have a bitter taste. On this account, a pure soft water supply is highly important to the industry.

Canneries and starch works,[11] as well as other food products manufacturers, use large quantities of water and, of course, the first requirement consists of a sanitary supply. In starch works, however, which manufacture glucose or corn syrup, the water must be unusually free from mineral salts because the dilute solutions have to be much concentrated in the course of boiling down the syrup. This causes any impurities which were originally present to appear in the finished product in much more concentrated form. Furthermore, if the glucose solutions are to be bleached by passage through charcoal filters, any mineral impurities which they contain will tend to deposit on the surface of the charcoal, thereby seriously impairing its efficiency. The same difficulty is met with in the manufacture of sugar, and these industries, therefore, require a water supply of high purity.

Soap works use large quantities of water in the soap-boiling operations and since calcium and magnesium salts precipitate an insoluble soap, it is obvious that this industry requires water low in hardness to produce a high-grade product. Likewise the laundering industry, using large quantities of soap, will also require low-hardness water.

The importance of soft water to all the industries using soap will be evident from the amount of soap destroyed by hardness. It is estimated that 18 to 20 pounds of soap are consumed per 1000 gallons of water for every 100 parts per million of total hardness figured as calcium carbonate. This ratio will be even higher if the total hardness is low and it serves to show the high soap-consuming cost of hard water to these industries, to say nothing of the detrimental effect of the slimy precipitates on the value of the finished products.

Water for Steam-making—The chief industrial use of water aside from cooling purposes is in steam-making. Water for steam-making is more or less suitable depending on the type and quantity of impurities which it carries. The customary method of interpreting the suitability of a water for boiler use is based on its tendency to cause foaming, corrosion, and scale or incrustation, and the cost of treatment to eliminate these tendencies is a fairly reliable inverse index of its value for this and many other industrial purposes.

Priming and Foaming. Priming and foaming are probably the least understood of boiler phenomena. Priming may be defined as an ebullition so violent that water in the form of spray is carried from the boiler before its separation from the steam can take place. It is controlled by the relations of heating surface, evaporation surface, circulation, and working load, all of which are factors influencing the violence and rapidity of ebullition, and by such features as dash plates, water space, and steam space, which affect the probability of spray reaching the steam exits. Priming, as thus defined, is a matter of boiler design and operation, unless the water is very high in soluble solids content.

Foaming is the formation of bubbles upon and above the surface of the water.

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[11] See Chapter 36.

The less easily these bubbles break the higher will the foam rise. It may become so excessive that the bubbles, or films of water enclosing steam, pass out with the steam. Naturally priming, or a tendency to prime, is an important factor in excessive foaming but, aside from this, the difficulty with which the steam pushes through the surface film of water and separates from it is a controlling agency.

With nearly pure water, foaming is very slight and never sufficient to cause the loss of water with steam in a well-designed boiler. Nearly all impurities dissolved or suspended in water increase the foaming tendency, though no two substances may do so to the same degree. As steam is used from the boiler, the impurities are concentrated and finally a stage is reached which will cause excessive foaming. If, therefore, the quantity of impurities and the effect of each were known, the calculation of the foaming tendency of a water would be a simple matter. Unfortunately, our knowledge of these factors is limited.

Suspended solids undoubtedly have an influence on foaming tendency, but it is practically impossible to predetermine the quantity of suspended matter in a boiler at any time. Turbidity originally present in the water is largely precipitated, while additional suspended matter is derived from the precipitation by treatment agents of impurities in solution in the feed water. Although both these classes of substances are undoubtedly important, the effect of precipitated magnesium being especially noteworthy, their role in inducing foaming cannot be predicted from an analysis of boiler feed water.

The dissolved impurities in a boiler water are usually regarded as the more important factors contributing to foaming. As the boiler water becomes more concentrated, the relative proportion of sodium and potassium salts present increases until all other dissolved substances become relatively insignificant in amount. It is, therefore, customary to attribute foaming primarily to sodium and potassium, since these substances are highly soluble and their relative importance in different waters is easily determined from analysis.

The usual remedy for foaming is blowing off a portion of the highly concentrated water and replacing it with fresh feed water. The locomotive boiler is a type likely to give trouble on account of foaming and offers, therefore, a satisfactory basis for an arbitrary classification of waters according to their foaming tendency. A non-foaming water may be defined as one that can be used in a locomotive boiler throughout one week's work without foaming; a semi-foaming water as one that will require one complete water change not oftener than every two days; and a foaming water as one that cannot be used so long as two days in a locomotive boiler without blowing off or changing water to prevent foaming.

Corrosion. Corrosion is one of the most harmful effects of impurities in water, and is due to free acid or to acid formed by the hydrolysis of salts in the water, or, in rarer cases, to acid formed by hydrolysis of fatty lubricating oils and to free oxygen. Of the harmful metal radicals magnesium is the one most likely to occur in quantity in natural waters, and when this occurs, in conjunction with such negative radicals as chloride or sulfate, the water will probably be corrosive in proportion to the quantities present.

One of the first occurrences in a boiler using untreated water is the precipitation of at least a part of the carbonate and bicarbonate radicals as calcium carbonate. Such precipitates can be acted upon by free acid, and to some extent by acids formed by hydrolysis, thus tending to neutralize them. The extent of this action is not well defined but it certainly offers some protection. More positive protection is usually secured by addition of alkali to the feed water to neutralize acidity, and an anti-oxidant to remove free oxygen.

Scale Formation. The formation of scale in boilers is a common effect of the use of impure untreated feed water. This phenomenon is the result of heating the water to a high temperature and concentrating it. The heat drives carbon dioxide out of the water, thus converting bicarbonate radical to normal carbonate and causing the precipitation of insoluble carbonate salts, especially calcium carbonate. Concentration will gradually increase the amount of dissolved matter to saturation, after which additional evaporation will cause it to pass out of solution. Suspended matter and colloidal matter, especially silica, are also largely deposited within the boiler.

Almost all natural waters, if used in a boiler for a great length of time without cleaning, would produce scale or sludge. As boilers are usually operated, temperatures and concentrations are permitted which result in the precipitation of practically all suspended and colloidal matter, all iron, aluminum, and magnesium, and all calcium to the full extent of its ability to combine with carbonate, and sulfate radicals. The iron, aluminum, and magnesium appear in the scale as oxides (magnesium carbonate may be present, but is not likely to be found in quantity in scale from high-pressure boilers), while the calcium may be present as calcium carbonate or calcium sulfate (a hydrated calcium sulfate frequently occurs, but in the modern high-pressure boiler its quantity is sufficiently small to be neglected). Whether these results are caused by a series of reactions or by a single chemical change is of little moment in connection with boiler calculations. The following reactions, therefore, are presented not as formulas for the changes which actually take place, but as equations which express the ultimate results of incrusting changes that occur within the boiler operated on untreated water.

$$\begin{aligned}
2Fe''' + 3H_2O &= Fe_2O_3 + 6H;\\
Mg'' + H_2O &= MgO + 2H;\\
Ca'' + CO_3 &= CaCO_3;\\
Ca'' + 2HCO_3 &= CaCO_3 + H_2O + CO_2;\\
Ca'' + SO_4 &= CaSO_4.
\end{aligned}$$

Scale may be of varying hardness, from a soft sludgelike deposit which can be flushed out, to a cement-like substance which must be chiseled out, depending on the character of the impurities in the water. In general, colloidal matter, especially silica, contributes to dense scale formation, as does also calcium sulfate. Of these substances, the one which is likely to occur in serious quantities is calcium sulfate. This material, contrary to the general rule, is less soluble in hot than in cold water. Hence as the temperature increases the calcium sulfate becomes less soluble and tends to come out in the form of scale aside from the effect due to the concentrating action of evaporation. In general, a water low in silica and sulfates will be low in hard scale-forming tendency and vice versa.

Classification of Waters for Boiler Use. The net value of a water for steam-making purposes will take into account the combined effects of foaming, corrosive, and scale-forming impurities, and on this basis, the committee on water service of the American Railway Engineering and Maintenance of Way Association have offered a classification of waters in their raw state that may be employed for approximate purposes, but, as their report[12] states, "it is difficult to define by analysis sharply the line between good and bad water for steam-making purposes."

The limit of 0.8 pound of incrusting and corroding constituents per 1000 gallons for the class of good waters restricts perfectly acceptable natural waters to a smaller number, but the choice of that figure was probably influenced by the fact that the incrustants in poorer waters can usually be reduced to that amount by proper treatment. The limits must be interpreted liberally in practice, because they are modified by the comparative hardness of the incrustation and the varying extent of corrosion effected by waters of the same mineral quantity content but of different chemical composition. Waters of the worst class may be improved by treatment in softening plants. A summary of boiler water classification is given in Table 3.

TABLE 3—APPROXIMATE CLASSIFICATION OF WATERS FOR BOILER USE

Incrusting and Corroding Constituents. Pounds per Thousand Gallons		*Classification*	*Foaming Constituents. Pounds per Thousand Gallons*		*Classification*
More than	*Not more than*		*More than*	*Not more than*	
....	0.8	Good	....	1.2	Good
0.8	1.7	Fair	1.2	2.1	Fair
1.7	3.7	Poor	2.1	3.3	Bad
3.7	5.7	Bad	3.3	......	Very bad

PURIFICATION OF WATER SUPPLY

Since natural waters contain many impurities, and since modern, domestic, and industrial requirements are so rigorously established, it is becoming increasingly necessary to purify natural waters, and a systematic technique has been developed for this purpose.

Volatile and oxidizable impurities are removed by aeration in fountain, spray, or cascade; suspended impurities, including much of the bacterial and microscopic contamination, by settling, coagulation, and filtration; residual microorganisms by chemical or other sterilization; soluble impurities (primarily of industrial importance) by preheating, lime soda, or zeolite treatment.

Volatile and Oxidizable Impurities—Natural waters always contain dissolved gases, such as oxygen and nitrogen and carbon dioxide from the atmosphere. In addition, they frequently contain undesirable gases and odors which have originated from decomposing matter in the water. These undesirable odors may usually be removed by purging the water with fresh air through the medium of natural stream flow or artificial aeration.

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[12] Am. Ry. Eng. Assoc. Const. and Maint. Sect. of Assoc. Am. Rys. Manual, Sect. 13, p. 66 (1936).

Natural aeration takes place slowly in slow-flowing streams but rapid-flowing streams, especially with cascades or water falls, quickly absorb much oxygen from the air, not only eliminating undesirable gases but at the same time oxidizing polluting substances, ferrous iron, etc., if they are present.

Artificial aeration is frequently used to supplement natural agencies. This may be accomplished by causing the water to flow over cascades or baffles, thus spreading it in a thin layer, or by passing it through fountains, throwing it into a spray, or by running it through trickling fillers causing increased surface exposure. The last is also of special value for oxidation of manganese and iron.* Such methods frequently greatly improve the quality of natural water.

Where aeration is used to oxidize and precipitate iron, tricklers are often used to good advantage. These are porous beds of broken stone, coarse sand, coke, shavings, or similar insoluble material having a large surface as compared to volume, through which the water slowly percolates. The air in such beds should be continuously or frequently changed, otherwise the process fails. Considerable attention is being paid of late to the design of spraying nozzles, possibly because of their extensive use in sewage purification. One type, installed at the Kensico reservoirs of the New York supply, is cast with spiral vanes which impart to the water flowing through them a whirling motion, said to be effective in accomplishing aeration.

Suspended Impurities—Suspended impurities, including turbidity from organic as well as inorganic matter, may be reduced by methods varying in efficiency, such as settling, coagulation, and filtration.

Settling—When water is impounded in reservoirs, suspended impurities gradually settle out, with the exception of living organisms which are floated by the gases they generate. When the reservoir can be constructed large enough and when microscopic growths do not develop, natural subsidence is frequently sufficient to produce clear water. The period necessary for accomplishing this result varies from a few hours to several days, and to be efficient for such purposes, basins should be at least 8 feet deep to avoid scouring of the material from the bottom by wind wave action.

Coagulation—When impounding alone is insufficient or too slow, sedimentation may be hastened and improved by the addition of chemical agents. For this purpose coagulants are employed, such as salts of iron or aluminum, which will produce a coagulable precipitate of hydrate by reaction with the carbonate radical already present.

When such a precipitated hydroxide is formed in the water, it adsorbs and encloses suspended impurities, including bacteria, and causes these to settle much more readily. The reaction and coagulation, however, involve a time element and unless two hours or more are allowed for the precipitation, it may not be efficient or successful. Much longer retention in the coagulating basins is often found advantageous. Such coagulation basins are usually from 12 to 15 feet deep and the rate of flow through them is limited to 2½ feet per minute. Baffle plates are often inserted to improve the mixing. The process usually removes 90 per cent or more of the total turbidity and 75 per cent of the bacteria.

Filtration—When settling alone is too slow or incomplete, filtration of the water is often resorted to. The usual filtering medium is sand and the method of application may be slow-sand, or rapid-sand, with or without pressure.

The first use of sand for filtration was made in London, more than a century ago, in 1829. A bed of sand some 12 feet deep was used and proved so efficient in removing turbidity that the system was considered a complete success. It was later noted that the death rate from typhoid fever was materially reduced, although it was not until long afterward, when the science of bacteriology had been developed, that the true explanation was understood.

The art of purifying water by filtration has developed from a simple procedure on a small scale to a complicated and extensive process. Whereas individuals and industries were once content with a comparatively clear water, they now demand a product colorless, free from suspended impurities, as nearly sterile as efficient operation will produce, and free from such quantities and varieties of mineral constituents as will affect its use for a particular purpose.

Slow-sand Filtration—The English, or slow-sand method (Figure 1) of filtration employs a water-tight basin containing about 5 feet of filtering material.

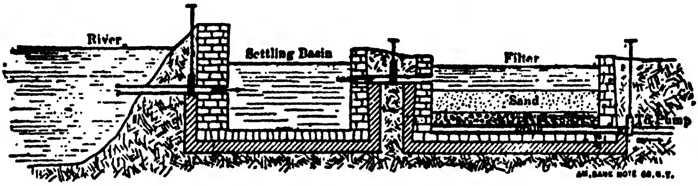

FIG. 1.

A common practice is to use 3 feet of fine sand at the top of the filter bed, below that about a foot of coarser sand supported on about 18 inches of graded gravel, the coarsest material at the bottom. Suitable drains are provided below the gravel to carry off the filtered water. Briefly, the operation of a slow-sand filtration plant is as follows:

The raw water containing suspended impurities, clay, bacteria, and microscopic plants, flows into a sedimentation basin. The impurities in part settle to the bottom either by gravitation alone, or, in some installations, aided by the use of a coagulant that agglomerates the particles and hastens the settling. The partly clarified water flows from an outlet near the top of the basin to the filter bed, which, after accumulating a surface skin of impurities, passes an effluent substantially free from suspended matter, including bacteria, at the rate of from one to three million gallons per acre per day. When the surface layer, or *Schmutzdecke*, becomes so thick that the rate of filtration is too low for economical operation, the surface layer of sand is removed and washed, and later replaced. This method is suited to purifying waters of low turbidity on a large scale. When used, it is usually for municipal water supplies.

Rapid-sand Filtration—The rapid-sand, or American, system (Figure 2) of filtration is adapted to the treatment of turbid and highly colored waters and is often employed where softening, as well as filtration, is necessary. The main differences between this and the English system are the artificial formation of a surface filtering layer on the sand by coagulation, the method of cleaning the filters by forcing a current of water, or in some cases air and water up through the filtering medium, and a much higher rate of filtration. Usually the rate is 125 million

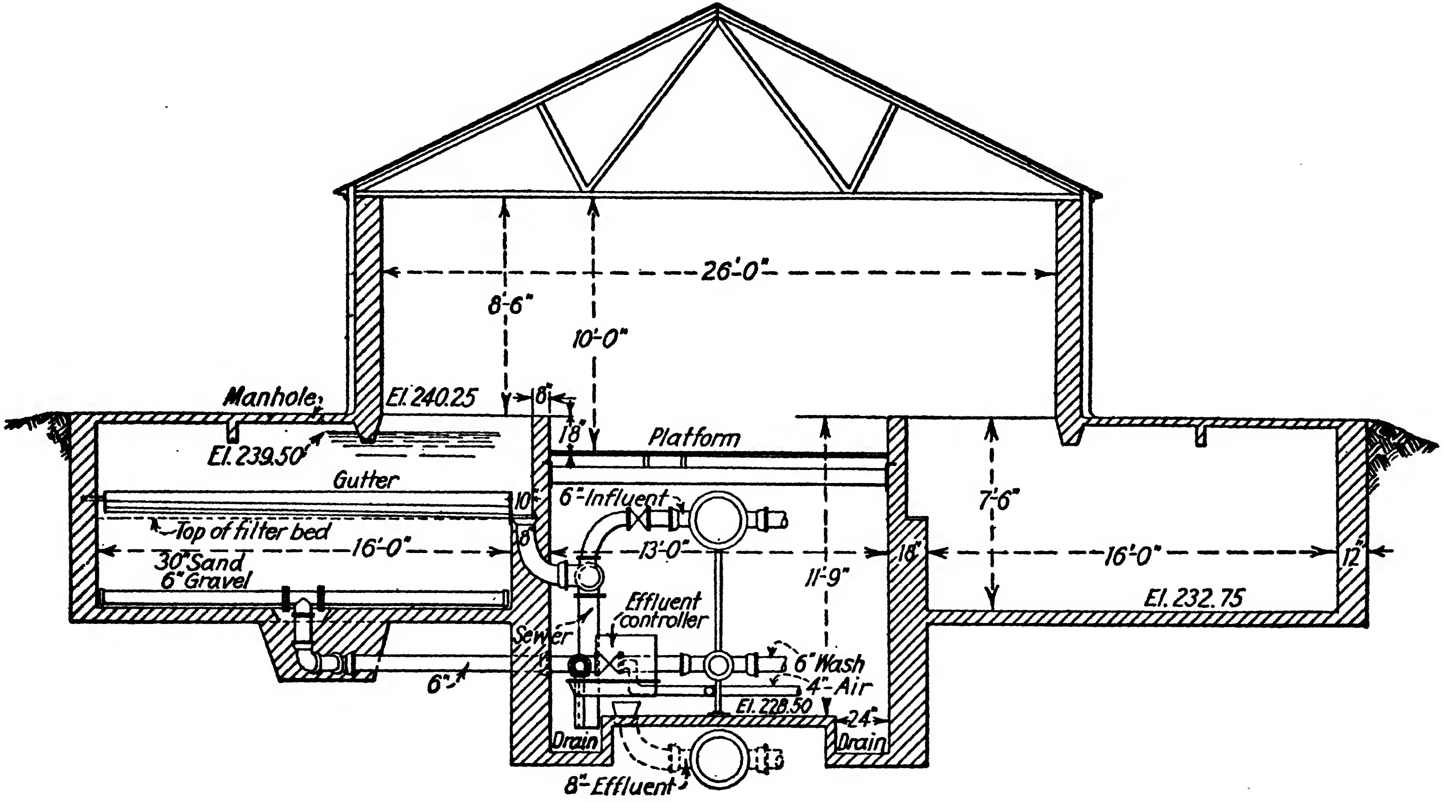
26'-0"
8'-6"
10'-0"
Manhole
El. 240.25
8"
18"
Platform
El. 239.50
Gutter
10"
6"-Influent
Top of filter bed
8"
16'-0"
13'-0"
30" Sand
6" Gravel
Effluent controller
11'-9"
7'-6"
18"
16'-0"
12"
El. 232.75
Sewer
6"
6" Wash
4"-Air
El. 228.50
24"
Drain
Drain
8"-Effluent

FIG. 2.

gallons per acre per day or about sixty times as fast as the English system. Machines to apportion automatically the dose of chemicals to the flow of water are necessary. These may handle the chemicals in solution or dry, but modern practice favors dry handling in large plants. A mixing and reaction chamber is provided to secure the proper coagulation.

The mixing basin used in this type of plant is frequently deeper than that in the slow-sand type, and is provided with baffles designed to secure maximum mixing or coagulation in minimum time. The filters in a large installation consist of concrete basins (in smaller ones wooden or iron tanks) with an area of 1500 to 2000 square feet, hence capable of handling four to six million gallons per day. They normally contain 30 inches of sand on a foot of graded gravel, the gravel resting on perforated strainers through which the water passes to the drain system and thence to the storage basins. Valves are provided for reversing the flow of water through the strainers and forcing it up through the filter bed, thoroughly stirring up the sand and washing the surface layer of impurities, which flow into channels provided to waste the dirty waters.

The operation of a typical plant where coagulation and filtration are practiced on a large scale is as follows:

The raw water passes through a Venturi meter, which records the volume of water passing and controls the rate of addition of coagulant to the flow of water. From the Venturi meter, the water passes to a weir basin where the water is divided, one part going to the lime saturators for use in preparing the milk of lime, another over the alum weirs where the alum is introduced, and a third to the mixing tanks. The lime-saturated water, the raw water, and the alum solution are thoroughly mixed by a system of baffles in the mixing tank, and a part of the precipitated material is allowed to deposit in the settling basins. The filters remove the remainder, gradually clogging up and filtering more and more slowly. At the end of eight to twelve hours' operation, the valves are reversed and clear water is forced back at a rate of 7 to 10 gallons per square foot per minute for five to eight minutes or until the sand is all clear, but the supernatant wash water is still murky. It is important to retain this murky water so that when the filter is again put into operation it will redeposit on the sand surface the rudiments of a new *Schmutzdecke*. The sand thus prepared is ready for another period of several hours' filtration.

Proper coagulation is a prime requisite in plants of this type. Some few waters contain sufficient iron to produce a good floc when lime is added, but most of them require the addition of filter alum, $Al_2(SO_4)_3$, although they may have sufficient alkalinity to precipitate the aluminum hydroxide without lime. In general, ten to thirty-five parts per million of alum are found necessary and the alkalinity must be sufficient to precipitate this as hydroxide. Several large plants have found it more economical to make their own filter alum by treating crude bauxite with sulfuric acid and using the mud or syrup directly for coagulation, thus obviating the necessity for crystallization, purification, etc., and some plants use iron sulfate instead of alum.

Coagulants other than alum are sometimes advantageous. Alum introduces sulfate radical to the water and when used with lime the combination increases the permanent hardness. To avoid this, sodium aluminate may be used. This compound introduces both aluminum and alkalinity at the same time and in dilute solution is readily hydrolyzed to give the alumina floc and leave only sodium in solution. This does not increase hardness but increases total dissolved solids by a small amount. To reduce even this small addition, peptized aluminum hydroxide or the more stable peptized ferric hydroxide may be used. If pure ferric hydroxide dispersion could be added, then when it coagulated and settled out no soluble addition would remain. The nearest approach to this reagent which has yet been commercially available is a dispersion of ferric hydroxide containing a small amount of ferric chloride to prevent coagulation during shipment. When this reagent is added to the water the ferric chloride content is quickly hydrolyzed to ferric hydroxide and the entire reagent coagulates. The only soluble residue is the chloride ion from the small amount of peptizing agent.

Pressure Filters—Many industrial plants have found it advantageous to use a type of filter that can be installed directly in the pressure water-supply system because of its conservation of water pressure, ease of installation, small space requirement, and flexibility in quantity of output. It has been further demonstrated that with the refinements of careful regulation and control of rate of filtration, addition of reagents, and systematic washing, these filters can produce an effluent comparable with many of the larger and more costly rapid-sand plants of the gravity type.

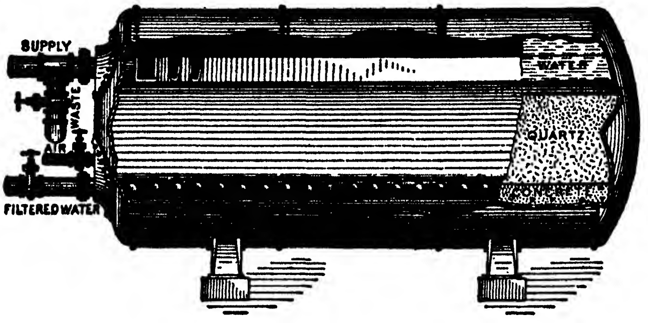

Fig. 3.

Pressure filters are usually stout steel tanks, cylindrical in form, placed with axis either horizontal or vertical. For installations requiring more than 40 sq. ft. area it is more economical to place them horizontal. The water is forced through the sand under pressure, but in other respects pressure filters differ but little in principle from the rapid-sand filters already described. See Figure 3.

By increased pressure, such a filter can, in an emergency, more than double its output with little effect on the quality of the filtered water. This is an advantage from an industrial standpoint. It has also been stated, with at least some degree of truth, that combined with sterilization, a water can be produced which will meet most of the exacting demands of a domestic supply.

Organic Contamination—Sedimentation and filtration serve to remove practically all suspended matter, including microscopic and bacterial organisms, but there are conditions when a separate or sometimes supplementary treatment is required.

Copper Treatment—If a source of supply develops too high a number of microscopic organisms, the filtration plant will require too large an amount of wash water and it is therefore necessary to treat these organisms in the reservoir before filtration to reduce their numbers.

In reservoirs open to sunlight, either before or after filtration, microscopic organisms may produce an unpleasant taste and odor from the essential oils which they develop. This may be avoided by the use of copper sulfate, which combines with the green coloring matter of the organisms and precipitates them to the bottom of the reservoir. Since the growth usually occurs near the surface, the copper sulfate is often applied by dragging sacks of the sulfate back and forth across the surface and using a quantity to give an ultimate concentration of about 0.5 p.p.m. This treatment when properly applied effectively eliminates the growth of microscopic organisms.

Chlorination—For the removal of residual bacteria, chlorine treatment has been used since about 1900. It was first applied on a large scale in the United States in 1908 for treatment of the Jersey City Water Supply at Boonton reservoir, when 40,000,000 gallons per day were treated with hypochlorite[13] of lime. By 1911 its use had been applied to 800 m.g.d.[14] and in 1918 to over 3000 m.g.d. Liquid chlorine[15] was successfully applied in 1912 and has since largely displaced bleach, until it is now in use in more than 3000 cities in the United States.

Liquid chlorine, because of its many advantages, is being used in most of the newer plants. Its germicidal effect, like that of chloride of lime, is due in part at least to the liberation of nascent oxygen. The chemical reactions with water may be represented as follows, showing the production of hypochlorous acid and nascent oxygen, both of which are probably powerful germicides:

$$Cl_2 + H_2O = HOCl + HCl$$
$$HOCl = HCl + O$$

Liquid chlorine may be purchased 99.8 per cent pure in steel cylinders containing 100 pounds, or 1 ton, at pressures which vary with the temperature from 50 to 200 pounds per square inch. It is also available in tank cars though it is seldom used in this type of container by water works. Anhydrous chlorine is not corrosive, but in the presence of a small amount of moisture it reacts vigorously with the ordinary materials of construction. This difficulty has been successfully overcome in several types of apparatus now in efficient operation by suitable valves which confine the water and water vapor to those parts of the apparatus constructed of non-corrosive material. These machines are constructed for either manual or automatic control and for direct application of the gas or a solution thereof.

Probably the best method of overcoming the corrosive tendency of chlorine gas and of obtaining a good mixture is the so-called minor flow system, in which a small portion of the total flow to be treated is diverted through a corrosion-resistant pipe or channel where it receives a concentrated dose of chlorine sufficient for the entire flow. This small portion is then fed back into the main flow, where it mixes and accomplishes the desired results without trouble.

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[13] For a discussion of the production of hypochlorites, see Chapter 11.

[14] Million gallons per day.

[15] For a discussion of chlorine production, see Chapter 10.

The operation of the Dunwoodie chlorinating plant, capable of treating 400,000,000 gallons of water per day for the city of New York, is typical of good operation. This plant has a total output capacity of a ton and a half of chlorine per twenty-four hours, the chlorine being applied automatically to the water by the direct-feed system through carborundum diffusors. Platform scales, each with a capacity of ten cylinders, are used to check the delivery of chlorine by weight. The apparatus is guaranteed to deliver within 5 per cent of the indicated chlorine and on check with the scales is found to have an error of less than 1 per cent.

The following advantages are claimed for liquid chlorine over chloride of lime treatment:

1. Liquid chlorine is more efficient and economical.
2. Liquid chlorine is a chemically pure substance.
3. A minimum space is required for storage and operation.
4. The disagreeable odors of open vats are eliminated.
5. Liquid chlorine does not decompose in storage.
6. Liquid chlorine may be handled effectively at low as well as high temperatures.
7. Liquid chlorine is susceptible of more accurate feed control.
8. No lime salts are introduced into the water.
9. Labor costs are materially reduced.

Bleaching Powder—Bleaching powder[18] is still used in a few plants in spite of the advantages of liquid chlorine, although of 6000 city water chlorinating plants in the United States less than 20 were still using hypochlorite in 1939.

Chloride of lime is soluble in water in the ratio of about one to twenty, but thorough mixing and treatment with water is necessary to extract the greater part of the active material from the sludge which forms. Whatever the method of solution, it is ordinarily made up so that 1 pound of chloride of lime is used for each 100 gallons of water and applied at some point in the system of purification where the organic matter has been reduced to the minimum and where a period of one-half to three or four hours can be given to allow the sterilizing action to go on.

The amount of chlorine, or of hypochlorite, necessary to effect sterilization depends on the amount of oxidizable material present, the temperature, the allowable time of reaction, the period of storage, and the turbidity of the water. If the dose is too heavy, disagreeable tastes and odors will be left in the water, while if the dose is too light, all the bacteria will not be destroyed. At some places excellent results are obtained with as little as 0.2 part per million of available chlorine, while under adverse conditions more than 1.0 part per million is sometimes necessary. A customary dose is 0.3 part per million. A recent type of high test hypochlorite has been placed on the market which is bringing the use of hypochlorite back into favor for certain purposes. This product[16] has the formula $Ca(OCl)_2$ instead of the old chloride of lime formula $CaClOCl$. It contains available chlorine not less than 65 per cent, which is about twice that of bleaching powder. The product is especially valuable for emergency chlorination

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[16] See Chapter 11.

of outlying local supplies, new pipe lines, repaired and relaid lines, control of algae, etc.

Ammonia—Ammonia[17] is often used in conjunction with chlorination, especially where taste and odor control are required. When ammonia is employed it is usually used at about one-half the rate of chlorine feed. It produces a chloramine compound which is much more lasting in the water and thus mantains a protective concentration of bactericide for a longer period of time in pipe line or reservoir. Its reaction rate on bacteria is probably not as nearly instantaneous as chlorine alone but the improvements in taste and odor are definitely recognized and the treatment is now widely used and recommended.

Active Carbon—Active carbon[18] is another material which is now being used for controlling taste and odor in water. The filtration of water through bone black has been practiced for many years where special table water or other high grade product was required but the use of activated carbon as an addition agent to the water is of more recent development. With some of the now available highly active chars the addition of 1 to 3 p.p.m. to the water before passing through the sand filters will serve to effectively eliminate objectionable tastes and odors. With certain types of very positive tastes much larger doses have been found necessary but it is claimed that when used in proper quantity active carbon can remove them all. One special type of application which is being developed consists of super-chlorination, i.e., addition of an excess of chlorine to not only destroy living organisms but other organic impurities as well, followed by filtration through active carbon which then eliminates the decomposition products and any residual chlorine giving a palatable water.

Ultra-violet Ray Sterilization—One development in water sterilization depends on the action of the ultra-violet rays emitted from an electric mercury vapor lamp immersed in the water to be treated. Details of construction vary, but the more efficient types use a quartz tube with mercury electrodes, the whole separated from the water by a second quartz envelope which prevents cracking of the tube by differences of temperature between the water and the lamp. Baffles are arranged to secure repeated passage of the water in thin films past the source of light. If turbid, the water must be clarified, otherwise the suspended matter may act as a protective medium, shutting off the light from the bacteria to be destroyed.

Some of the more recent lamps have been fitted with arrangements whereby the water will, in case of an interruption of the current and the light going out, be automatically shut off and not turned on again until the lamp is lighted and has regained its maximum efficiency.

The advantages of ultra-violet sterilization are largely aesthetic. No chemical is added to the water and no tastes or odors are developed. The water can be heavily overdosed without affecting its quality, but cost of operation demands a very careful control to secure complete sterilization on the one hand and a reasonable current cost on the other.

Ozone—Although the oxidizing power of ozone has been known for some time, it was not used for water sterilization in appreciable amounts before 1908. The cost of ozone treatment is usually prohibitive but its use for special cases is

[17] For a discussion of ammonia production, see Chapter 8.

[18] For a discussion of the preparation of active carbon, see Chapter 18.

being promoted by several industrial groups. It produces an unusually palatable drinking water and for this particular purpose may frequently warrant the high cost. It is also advocated for treatment of recirculated swimming pool water since, due to its slight solubility, overdosing is impossible and irritation of the mucous membrane so prevalent in chlorine treatment is avoided, but unless it is properly diffused through multiple outlets throughout the pool its efficacy is not established except at prohibitive cost. For efficient operation, the air which is ozonized and later applied to the water is first dried by passing through towers of some desiccating material or by artificial refrigeration. The voltage used in producing the silent electrical discharge for ozonization must not be allowed to rise too high, otherwise sparking occurs with a resultant waste of power, heat-decomposition of the ozone, and the formation of oxides of nitrogen that hinder the production of ozone. Efficiency furthermore demands a thorough mixing of the raw water and ozonized air with recovery of any ozone not absorbed in the mixing chamber.

DISSOLVED SOLIDS

The removal of volatile suspended and organic impurities from natural waters by aeration, filtration, and chlorination usually accomplishes sufficient purification for sanitary purposes, but for industrial applications it is frequently necessary to reduce or eliminate certain soluble impurities, particularly calcium, magnesium, and iron, in order to meet the requirements of specialized plants. For this purpose, preheating, lime-soda precipitation, zeolite treatment, or distillation are used.

Preheaters[19]—In connection with boiler operation, steam is often available at low or negligible cost for operation of feed water preheaters which serve the double purpose of conserving heat and boiling out oxygen and carbon dioxide, thus converting bicarbonate to normal carbonate. The gases begin to come off at 65° C., and at the boiling point expulsion is very nearly complete. The results which follow will depend on the quantitative relationship which the particular basic radicals bear to the carbonate radical at these temperatures. The most important effects are removal of the corrosive oxygen and reduction of the scale forming calcium carbonate down to its limit of solubility, say 40 to 50 p.p.m. Treating chemicals may be added in the preheater and, when properly applied, will greatly improve the results obtained.

Preheaters are of two general types, open and closed,[20] and since they may function not only to purify the feed water but frequently to conserve heat as well, they are very widely applied in industry.

Lime-soda Water Softening—When preheating is used to convert bicarbonates to normal carbonates, further treatment with lime is usually of little value unless the magnesium content remains high. Sodium carbonate will be useful, however, to convert any soluble salts of calcium to the less soluble carbonate. When chemical treatment is to be applied, without preheating, both lime and soda ash are used in most cases.

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[19] For a discussion of the principles of heat transfer in this type of equipment, see Chapter 2.

[20] For a discussion of preheaters and economizers the reader is referred to "Boiler Management, Maintenance and Inspection," H. C. Armstrong and C. V. Lewis, Lippincott Pub. Co. (1937).

Lime-soda treatment is used alone or in conjunction with alum coagulation for purifying water supply on a large scale. When slaked lime is added to water, it supplies hydroxide ions which are appropriated in order by free acids, aluminum, iron, half-bound acid (bicarbonate), and magnesium, thus:

$$\begin{gathered}(\mathrm{OH})^{-} + (\mathrm{H})' \rightarrow \mathrm{H_2O}\\ 3(\mathrm{OH})^{-} + (\mathrm{Al})''' \rightarrow \mathrm{Al(OH)_3}\\ 2(\mathrm{OH})^{-} + (\mathrm{Fe})'' \rightarrow \mathrm{Fe(OH)_2}\\ (\mathrm{OH})^{-} + (\mathrm{HCO_3})^{-} \rightarrow \mathrm{H_2O} + (\mathrm{CO_3})^{--}\\ 2(\mathrm{OH})^{-} + (\mathrm{Mg})'' \rightarrow \mathrm{Mg(OH)_2}\end{gathered}$$

These changes result in neutralization of free acid, such as free carbonic acid or hydrogen sulfide, precipitation of aluminum, iron, and magnesium as hydroxides, and conversion of bicarbonate to normal carbonate. Simultaneously, the calcium salts of all the corresponding acids are formed and all are soluble except the normal carbonate. Therefore, the hardening constituents, iron, aluminum, and magnesium, when precipitated, will be replaced in solution by calcium without any net reduction in hardness, except insofar as these constituents may have been associated with bicarbonate.

The bicarbonate, or acid carbonate, however, is converted to normal carbonate by neutralization with calcium hydroxide, as indicated above, and each two hydroxide ions (associated with one calcium ion) produce two carbonate ions (capable of precipitating two calcium ions). Therefore, an ion of added calcium and an ion of calcium already in solution are precipitated with each ion of bicarbonate originally present, down to a concentration of thirty parts per million, which is the limiting solubility of calcium carbonate under the circumstances. Other calcium salts which may have been originally present or may have resulted from precipitation of iron, aluminum, or magnesium will remain in solution and cannot be precipitated by further additions of lime.

Results of Lime-Soda Treatment—The net results, therefore, which may be accomplished by addition of calcium hydroxide will be precipitation of iron and aluminum, and reduction of magnesium to about six or eight parts per million, reduction of carbonate to about thirty parts per million of calcium carbonate, and conversion of other acid radicals to their soluble calcium salts, except such as may have been already associated with calcium or alkali. The amount of lime which may profitably be added will, therefore, be the equivalent of the free acid, iron, aluminum, magnesium, and bicarbonate.

When soda ash is added to water which has already been properly treated with lime, it supplies carbonate ion which unites with the calcium ion, thus:

$$(\mathrm{Ca})'' + (\mathrm{CO_3})^{--} = \mathrm{CaCO_3}$$

This results in the precipitation of calcium in the form of carbonate down to about thirty parts per million. Simultaneously the sodium salts of the acid radicals are formed and remain in solution.

The net result, therefore, which may be accomplished by addition of sodium carbonate after lime treatment will be reduction of calcium to about thirty parts per million of calcium carbonate, leaving in solution the original content of all other acid ions in the form of their sodium salts.

The amount of soda ash which may profitably be added will, therefore, be the equivalent of the calcium remaining in solution after lime treatment. This in turn is equivalent to acid ions other than carbonate less any alkali which may have been originally present.

Use of Barium Carbonate—The use of soda ash to supply the carbonate radical for water-softening results in an increase in the highly soluble constituents, for the sodium thus added remains in solution. Soda-lime treatment is extensively used in many types of plants but in some industrial uses of water a great increase in content of sodium is accompanied by undesirable effects. In such cases it may be necessary to use, in place of soda ash, some carbonate whose base will not be held in the dissolved system by $SO_4^{=}$ or Cl^{-} radicals. No commercial compound that will wholly fulfill these conditions has been used. Barium, Ba'', however, will not remain in solution with $SO_4^{=}$ radical. Barium carbonate, $BaCO_3$, therefore, possesses a distinct advantage over soda ash in the treatment of waters high in sulfate and is used in isolated cases. It is itself nearly insoluble but can be added to the water in suspension, any excess above the amount required for the reaction being removed with the precipitate. It has the disadvantage of a comparatively high price and a poisonous character prohibiting its use in potable waters.

Prevention of "After Deposits"—Successful softening plants are so designed that the chemicals and water are thoroughly mixed, that adequate time for the reactions is allowed, that a suitable sedimentation compartment is traversed by the water before filtration, and that a final rapid filtration will remove the remaining matter in suspension. Neglect of any one of these features will make the best results incapable of attainment. If the reactions are incomplete when the water leaves the softener, "after-deposits" of precipitates are likely to occur, causing much trouble. To prevent this, softened waters are sometimes treated with carbon dioxide, which will hold in solution the calcium and magnesium which would otherwise form after-deposits. This practice is to be commended as a preventive of deposits in the cold, but the material is thrown down in any case when the water is heated and the addition of carbon dioxide increases the corrosive action under some conditions. Carbonating softened water is, therefore, by no means a practice devoid of deleterious results.

Use of Softened Water—Softened water has many applications in the industries. It is also used for drinking purposes, for which it is doubtless better suited than many of the untreated waters. Inasmuch as barium salts are poisonous in comparatively small quantities, however, water treated with the carbonate or other salts of barium cannot be used for potable purposes.

METHODS OF LIME-SODA SOFTENING

The recognized standard method for the proper treatment of waters for softening purposes is that of adding to the water, in tanks designed for the purpose, chemicals in proportion to the amount and nature of the ingredients to be removed and the volume of water treated. The major portion of the precipitate formed is allowed to settle and the rest may be removed by filtration. When properly controlled by chemical analysis of the raw and treated water, this method can be made to satisfy all ordinary conditions.

There are two general types of such softeners—one known as the intermittent process, the other continuous.

Intermittent Softeners—Intermittent softeners employ tanks operating in pairs. They are filled alternately with water; while one is filling the reagents are introduced and are thoroughly mixed by mechanical stirring devices. Settling is hastened by stirring up the particles from a former treatment, which particles act as nuclei upon which precipitation may start and larger crystals form. By the time the tank is filled all the reagent has been added, the stirring is stopped, and the precipitate is allowed to settle. The clear softened water is drained from near the surface by means of a floating hinged pipe, so arranged that as the level of the water is lowered neither the surface scum nor the precipitate at the bottom is allowed to pass through. This materially lessens the duty of the filter through which the water usually next passes before use. Thus, while one tank is being used for reaction and settling, the other is supplying treated water; the process being so regulated that a constant supply of soft water is always available. Sludge is disposed of when necessary by simply opening a sludge gate at the bottom of the tank and raking out the sludge. It is claimed for this type of softener that since definite quantities of water are treated each time and the exact amount of chemicals weighed out, it is possible to treat more accurately any water which may vary in quality.

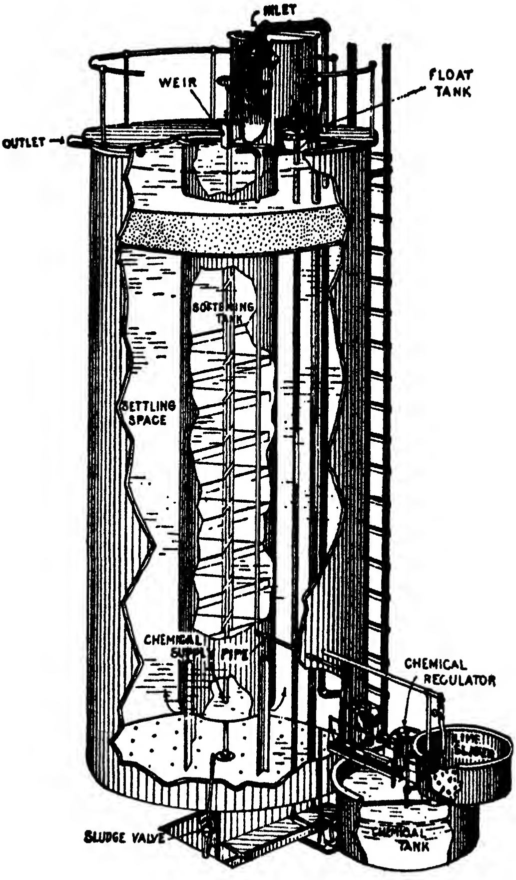

Fig. 4. Typical Lime-soda Water Softener—Continuous Type.

Continuous water softeners, as the name implies, differ from the intermittent in the use of a continuous feed of raw water and chemicals and a resulting uninterrupted flow of treated water from the softener. The details of construction vary to a considerable extent. A typical softener is operated from the ground level, where the preparation and mixing of the reagents can be readily inspected and controlled. See Figure 4. The tanks are usually built of steel. The raw water is pumped to the top of the softener and allowed to flow upon an overshot wheel which furnishes the power necessary to operate the mixing devices and chemical pumps. From the wheel the water passes over a raw-water weir into the top of the mixing chamber where it is treated with the proper quantity of chemicals, as regulated and operated by the flow of raw water. The mixing downtake is provided with a vertical shaft on which are mounted a number of paddles to secure vigorous stirring and intimate mixture of water and reagents. From the open bottom of this chamber the softened water slowly rises, allowing sufficient time for the precipitate to settle to the bottom of the softener, from which it is periodically flushed by opening a sludge valve provided for this purpose. By the time the softened water has reached the top, it should be practically free from suspended particles, but an excelsior wood-fiber filter is used to remove any remaining turbidity.

The advantages of the continuous softener lie mainly in its large output for small space required, low labor and attention requirement.

Hot process water softeners take advantage of the effect of heat in hastening and completing chemical reactions. Except for the addition of an arrangement for chemical feed, the construction and operation of these devices differ but little from open feed-water heaters.

When properly designed and operated to give adequate time for reaction, high enough temperature, accurate control of chemical feed, and proper filtration, this type of softener has several advantages for boiler feed water treatment worthy of mention. In the first place, it performs all the functions of an open feed-water heater; a decided saving in coal is thus effected. Condensed exhaust is returned to the softener with a resulting decrease in quantity of raw water to be treated. The use of only one reagent, soda ash, simplifies and hence tends to easier and better regulation of the chemical treatment. Proper heating effects the removal of the oxygen, free carbon dioxide and temporary hardness. The quantity of chemical necessary for purification is thus materially reduced. The accelerating action of the higher temperature has already been mentioned, and to this may be added that the reactions tend to go farther toward theoretical completion. The precipitates formed are more coarsely granular and hence settle more rapidly and completely. Where sufficient steam is available, these softeners, therefore, possess a decided advantage over others.

ZEOLITE OR PERMUTIT SOFTENERS

Softeners of the permutit type constitute an important development in the art of water softening. The peculiar properties of zeolites have been known for a long time and the possibility of their use in water softening practice was recognized as early as 1850, but their actual application on a commercial scale is an accomplishment of the twentieth century.

The permutits are either natural or synthetic base exchange silicates or zeolites of the following general type formulae:

$$Na_2O \cdot R_2O_3 \cdot xSiO_2 \cdot nH_2O$$

In this formula R_2O_3 stands for an amphoteric metal oxide, usually alumina or iron oxide; $xSiO_2$ stands for two or more molecules of silica; and nH_2O stands for various amounts of water of hydration.

These zeolites are insoluble in water but have the property of exchanging their bases by contact with solutions containing a different base. Thus, in water softening, a sodium zeolite will exchange with the calcium and magnesium in the hard water coming in contact with it, producing calcium and magnesium zeolites and water containing molecularly equivalent amounts of sodium salts in place of the calcium and magnesium salts originally present.

The following equations are typical of the reactions during the softening run, the hardness of water being due to the bicarbonates, the sulfates, the chlorides or the nitrates of calcium or magnesium or usually mixtures of two or more of these salts. In these type reactions, the complex zeolite radical is represented by the symbol Pm.

$$Ca(HCO_3)_2 + Na_2Pm = CaPm + 2NaHCO_3$$
$$CaSO_4 + Na_2Pm = CaPm + Na_2SO_4$$
$$MgCl_2 + Na_2Pm = MgPm + 2NaCl$$
$$Mg(NO_3)_2 + Na_2Pm = MgPm + 2NaNO_3.$$

The "exhausted" or calcium and magnesium zeolites can be regenerated to the "active" or sodium zeolites by treatment with a solution of common salt, a 5 per cent to 10 per cent NaCl solution usually being used. This "regeneration" is essentially a reversal of the preceding reactions and illustrated by the following type reactions:

$$CaPm + 2NaCl = Na_2Pm + CaCl_2$$
$$MgPm + 2NaCl = Na_2Pm + MgCl_2$$

In practice, the mineral is usually not run to complete exhaustion as the softening run is stopped when the effluent is no longer of zero hardness.[21] However, where a zero hardness effluent is not demanded, as in softening water for certain municipalities, it is common practice to overrun the zeolite softeners so as to yield a mixed effluent of the desired degree of hardness.

These zeolite softeners are built either in vertical or horizontal units of gravity or pressure type and in sizes ranging from small household softeners with a capacity of less than 100 *gpd* up to large multiple-unit industrial plants handling several million gallons per day. Figure 5 represents a single vertical unit and Figure 6 represents a single horizontal unit, both being of the pressure type.

During the softening run, the incoming hard water enters the top of the machine and flows downward through the bed of granular zeolite and the supporting layers of graded gravel, being collected at the bottom by means of a strainer system which delivers it into the service line. An electric alarm meter is usually used to signal the approaching end of the softening run and the exact end point may be quickly determined by a very simple soap test.

The exhausted zeolite bed is then given a brief backwashing by sending a current of water through it in the reverse direction to the softening flow. This upward flow cleanses and hydraulically regrades the granular permutit.

After backwashing, a measured volume of a saturated common salt brine is introduced into the softener by means of a hydraulic ejector which serves to lift and also dilute the brine to an approximately 10 per cent NaCl content. Following the brine charge, raw water is turned into the softener and this rinses the

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[21] Note that "zero hardness" does not mean that all salts have been removed, but only that the calcium and magnesium ions have been eliminated. All of the anions are still present in solution along with an equivalent amount of sodium ions.

waste salts downward to the drain. The disappearance of the waste salts is indicated by a simple soap test and the softener is then ready for another softening run. The complete operation of backwashing, regeneration and rinsing takes only about one-half hour to complete, the backwashing usually taking about 5-10 minutes, the brine injection 3-6 minutes, and the salt rinse 12-18 minutes.

The method of operation described above is that of a standard or downflow zeolite softener. Upflow, in which the incoming hard water flows upward through the softeners, has also been used, but is of a more limited applicability. Downflow softeners remove dirt from the water in the upper part of the permutit and backwashing removes this dirt from the softeners. Downflow softeners can therefore be used as a combination of filter and softener if the amount of dirt is not excessive.

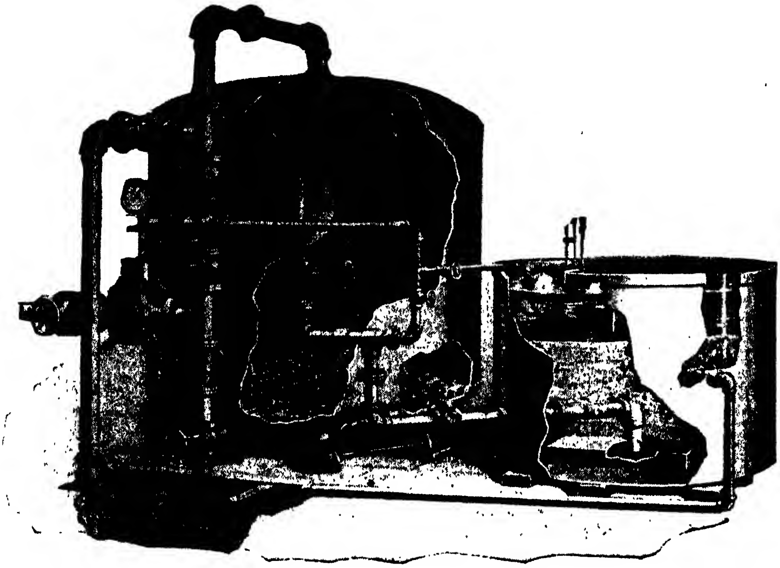

FIG. 5. Vertical Zeolite Water Softener.

Advantages of Zeolite Softening—The advantages of the zeolite process are many. It produces a water of zero hardness, is simple to operate, requires little space, is equally effective at all ordinary temperature ranges, is flexible in operation, can be used under pressure, thus avoiding double pumping, automatically takes care of variations in hardness in the raw water, and forms no sludge. The effluent produced is of a lower degree of hardness than can be produced by any other method of water softening excepting only distillation, but it cannot reduce the amount of dissolved solids in the water. A newer development has been its use in softening municipal water supplies and further it has proved feasible for household use.

Zeolite plants may be used to remove ferrous iron by base exchange in addition to hardness. Even after the zeolite stops producing zero hardness water, it still continues to remove ferrous iron by base exchange since the Ca zeolite exchanges its Ca against the Fe.

Costs of Zeolite Softening—The salt consumption on most ordinary waters amounts to one-half pound of salt per thousand grains of hardness removed. Such costs compare very favorably with the operating costs of the chemical types of water softeners. These costs vary depending on the composition of the water being treated and the local prices for chemicals, but, in general, it may be said that waters containing mostly permanent hardness are more economically softened by the zeolite process, while waters containing mostly temporary hardness are more economically softened by the lime treatment. With waters high in temporary hardness, the zeolite process is sometimes preceded by a lime treatment, this serving to precipitate and remove most of the temporary hardness and thus reduce the total dissolved solids. The remainder of the temporary hardness and all of the permanent hardness may then be removed by the zeolite process.

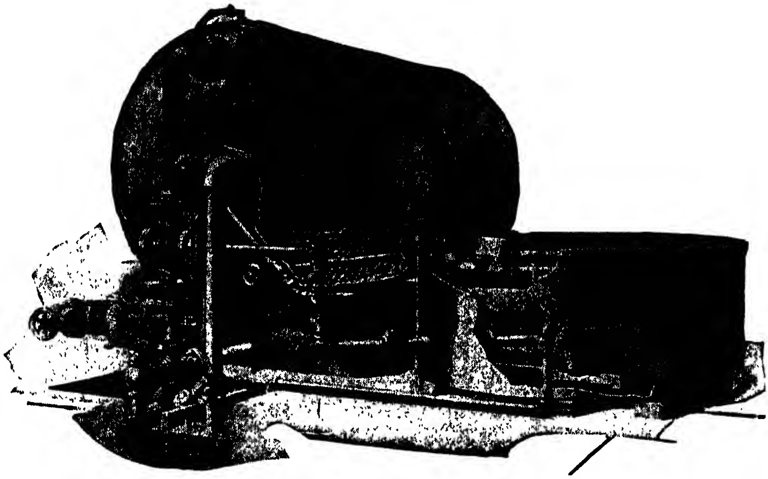

FIG. 6. Horizontal Zeolite Water Softener.

Organic Base Exchange Softeners—Synthetic resin base exchange compounds have recently been developed which function much as the zeolites in water softening. These resinous substances are made by sulfonating phenol-aldehyde condensation products.[22] The resins may be regenerated with hydrochloric acid and have the capacity to remove hardness.

Another type of product is made by the Permutit Company by sulfonating wood, lignite or the like.[23] Other types have been developed by E. L. Holmes [24] and W. A. Gibbons.[25]

Resins have also been developed for removing the negative ions, chloride and sulfate from water. Such a resin is made by M. C. Schwartz and W. R.

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[22] Richter, A., Ang. Chem. *52*, 679 (1939); U. S. Patents: Several, including 2,195,-196 (Mar. 26, 1940), to Wasseniger and Griessbach; Griessbach, R., Ang. Chem. *52*, 215 (1939).

[23] U. S. Patents 2,191,059 and 2,191,060 (Feb. 20, 1940).

[24] U. S. Patent 2,191,853 (Feb. 27, 1940).

[25] Canadian Patent 378,655 (Jan. 3, 1939).

Edwards, Jr., and G. Boudreaux[26] by condensation of *m*-phenylene diamine and formaldehyde.

The possibilities which these resins open up are such that we may soon hope to see a water treatment system in extensive use, wherein the positive ions are replaced by hydrogen and then the negative ions by hydroxide so that the major dissolved impurities in the water will be converted to HOH, i.e., more water, giving a product essentially free of all impurities. Such double systems of resin exchangers (one bed to remove the metallic cations, substituting hydrogen, the other removing anions, substituting OH^-) are already being used commercially to a limited extent[27] to produce water essentially as pure as distilled water.

DISTILLATION

Conditions exist where softening, filtration, and other purification processes are insufficient. Certain industries must have an absolutely pure water, and in some localities no water fit for domestic or industrial use is available. Under such conditions distillation is the only resort. Unless the double zeolite process mentioned above proves successful in economically yielding water of negligible impurities.

High cost of installation and operation is the main disadvantage of distillation, but where a high degree of purity is an absolute necessity, cost may become a secondary consideration. Such a case may be found in the manufacture of artificial ice where, for best results, all soluble matter must necessarily be removed, and distillation offers the most satisfactory method.

INTERNAL BOILER FEED-WATER TREATMENT

Water which is to be used for steam-making purposes must, of necessity, receive considerations which are different from those accorded to municipal or processing supplies. Steam boilers are essentially concentrators of the solutions of impurities present in the feed water and, as previously pointed out in the discussion of uses, these impurities may cause scale formation, corrosion, and foaming. It is desirable to have all impurities reduced to a minimum before the water enters the boiler but since the minimum cannot be nil, some sort of internal treatment must be given to the water within the boiler.

Internal treatment is not a serious problem when the boilers are operated at moderate pressures, say up to 250 pounds but modern practice is tending toward much higher pressures so that within the last decade more horse power has been installed at pressures above than below 400 pounds. At these pressures and corresponding high temperature, steam release per unit area is very rapid and water treatment for these conditions requires skillful control.

Scale forming elements include calcium, magnesium and, worst of all, silica. The calcium and magnesium may be largely reduced by external zeolite treatment, and external treatment with magnesium, iron or aluminum for silica removal has been practiced in a few large installations but in general, internal

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[26] Ind. Eng. Chem. *32*, 1462 (1940).

[27] Myers, R. J., Eastes, J. W., and Meyers, F. J., Ind. Eng. Chem. *33*, 697 (1941); Lindsay, F. K., Trans. Amer. Inst. Chem. Engrs. *37*, 547 (1941).

treatment for control of these constituents must also be applied. Formerly the use of soda ash was widespread. This reagent hydrolyzes at boiler temperatures to give a high concentration of hydroxyl ion which tends to prevent acid corrosion, and at the same time converts calcium and magnesium to carbonate or hydroxide compounds which give a soft scale. However, present practice is tending to the use of sodium phosphate.

At the temperatures encountered in high pressure boilers, phosphates precipitate calcium and magnesium as insoluble phosphate muds which accumulate as sludge in the mud drums of the boilers and hence do not form scale. If the magnesium concentration is high enough in proportion to silica, these muds also carry down most of the silica so that, under proper conditions, the boilers may be operated for months without scale formation. These non-scaling muds are removed from the boiler by periodic "blow down" periods during which the heavy sludge is blown out of the system. Many phosphates are available for use but it is generally conceded that whichever one may be used the desirable concentration of phosphate ion ($PO_4^{=}$) to be maintained in the boiler should be between 60 and 120 p.p.m.

Corrosive conditions due to acid hydrolysis of salts, such as those of magnesium and iron, may be successfully combated by maintaining a high alkalinity. This condition is also essential for the proper precipitation of phosphate sludge and it is now common practice to maintain a pH of 11.0 or higher depending on the boiler pressure and temperature. This high pH may be produced by utilizing a suitable phosphate mixture for the feed-water treatment. Thus, trisodium phosphate gives a higher pH than disodium which in turn is higher than monosodium phosphate. Use of one or more of these with or without added caustic soda will therefore suffice to give both the desired phosphate concentration and the desired pH.

Corrosion due to oxygen may be largely eliminated by effective preheaters which will boil out most of the dissolved oxygen from the feed water, but for complete control it is also essential to employ some reducing agent within the boiler. Tannates have long been effectively used for this purpose and still serve when it is desirable at the same time to introduce a colloidal agent. Many plants today, however, receive a treatment of sodium sulfite or colloidal ferrous iron for this purpose. A concentration of 10 to 20 p.p.m. of sulfite is regarded as adequate to ensure freedom from oxygen corrosion.

Foaming or carry-over is not serious with low pressure boilers but with the high speed generation and delivery of steam at high pressures there will be a carry-over tendency in spite of the advanced engineering design of steam purification equipment which should be an essential part of all high pressure installations. This tendency can be minimized only by keeping a low concentration of total dissolved solids in the boiler water. This is accomplished by blowing off a percentage of the boiler water which at the same time serves to carry off the sludge of precipitated solids. At low pressures the heat loss in this water may not be serious, but at high pressures it is desirable to conserve the heat by continuous blow-down through a heat exchanger or other heat conserving device. Usually, with ordinary types of feed water, the amount of blow-down will be from 2 per cent to 5 per cent of the feed water volume but in any case the total solids in the boiler water is seldom allowed to run higher than 3500 p.p.m.

Caustic embrittlement may be caused by high concentrations of caustic soda in boiler waters and is particularly aggravated by the presence of silica. It causes the steel of the boiler structure to become brittle and liable to crack, especially at points where the metal is under stress, and may be disastrous especially in high pressure installations. It is effectively prevented by maintaining a sufficient concentration of sulfate in solution in the water. The amount required depends on the amount of total alkalinity and on the boiler pressure. Recommended ratios are for pressures up to 150 pounds, 1 part of sodium sulfate to 1 part of alkalinity computed as sodium carbonate; for pressures up to 250 pounds, 2 of sulfate to 1 of alkali and for pressures above 250, 3 to 1. In many types of feed water this ratio will be automatically maintained by the nature of the constituents in the raw water but it should be maintained by additions of sulfate if necessary. Modern boiler design is eliminating the cracks and seams where in former designs high alkali concentrations could build up. Also modern feed-water treatment usually contains phosphate. It is now generally recognized that under such circumstances the fear of caustic embrittlement is largely allayed.[28]

APPENDIX

EXAMINATION OF WATER SUPPLY

The value of a water for industrial or domestic use depends upon its purity. Its examination, therefore, consists in a determination of the nature and quantity of the impurities present. The type of examination will depend on whether the water is to be used for sanitary or industrial purposes.

Special Sampling Methods—Special sampling methods have been developed to insure representative samples for analytical purposes. For microscopic study, the organisms are gathered with as little disturbance as possible and it is recognized that these organisms are usually present in much higher concentration near the surface of the water. For bacteriological examination the usual precautions to prevent contamination with unsterile apparatus are taken and further development of bacteria in the sample after it is collected is avoided by refrigeration and by reducing to a minimum the time interval between collection and analysis. For chemical examination where dissolved solids are to be examined, it is often necessary to collect the samples at a definite depth, and special devices, (Figure 7) have been designed to be lowered to any predetermined distance and then opened for obtaining of the sample. Where dissolved gases must be determined, devices (Figure 8) are used, insuring a thorough flushing out of the sample bottle before the accepted sample is taken.

SANITARY ANALYSIS OF WATER

A sanitary analysis of water ordinarily consists of physical examination for temperature, turbidity, color, and odor; microscopical examination for number and

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[28] For a discussion of new trends in feed water treatment, the reader is referred to Straub, F. G., Trans. Amer. Inst. Chem. Eng. *36*, 395 (1940); also Chem. & Met. Eng. *47*, 477 (1940).

kinds of microscopic organisms; bacteriological examination for total number and number of certain kinds of bacteria; and chemical examination, usually including total residue on evaporation, loss on ignition, fixed solids, alkalinity, hardness, chlorine, iron, nitrogen as albuminoid ammonia, nitrogen as free ammonia, nitrogen as nitrites, nitrogen as nitrates, and sometimes dissolved oxygen. Sanitary examination in general is of less industrial value than mineral analysis, though for water used in the food industries and for the control of purification plants, sanitary analysis is of prime importance.

MINERAL ANALYSIS OF WATER

A mineral analysis of such waters as are ordinarily used for industrial purposes includes four classes of water impurities: suspended solids, colloidal matter, dissolved gases and dissolved solids.

Suspended Solids—Suspended solids include all organic or inorganic matter that can be removed by filtering. This material is complex and consists of many chemical compounds not usually determined in detail. Two determinations are often made: turbidity, the figures for which indicate the concentration of a known standard suspended matter that will obscure just as much light as the water under consideration, and suspended matter, which is the proportion by weight of the suspended solids in the water. The ratio of suspended matter to turbidity is called the coefficient of fineness. The greater the value of this coefficient, the greater will be the average weight of the suspended particles, and hence the greater will be the ease with which they can be removed.

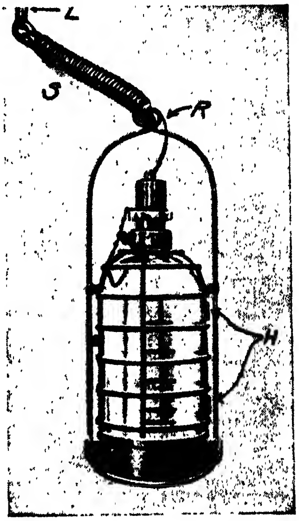

FIG. 7. Sampling Device. The outfit is lowered on a rope to any desired depth when a sudden jerk stretches the spring and pulls the stopper so that the bottle may fill.

Colloidal Matter—Colloidal matter includes, for the most part, silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3), though in some waters, especially polluted waters, a considerable amount of organic matter may be present in the colloidal state. In a mineral analysis, colloidal matter is not distinguished from that in true solution.

Colloidal matter, which is not in true solution, is so finely distributed that it does not usually contribute turbidity. However, in a water which contains no other suspended matter the presence of colloidal material may sometimes be detected by reason of a faint opalescence observable in brilliant light. For instance in the Ozark uplift there are many large springs and the term Blue spring [29] is applied to many of them. The blue color haze observable in the almost crystal clear depths of the springs is attributed to material dissolved by the water under great pressure and released as colloidal matter as the water rises to the surface outlet.

[29] Missouri Bureau of Geology and Mines, Second Series, Vol. XX, p. 344.

The Dissolved Gases—The dissolved gases, carbon dioxide (CO_2), hydrogen sulfide (H_2S) and oxygen (O_2) are not often determined, because the tests, to be of value, must be made at the source with special apparatus. The content of gases in stream waters is necessarily small, but in ground waters great quantities of gases may be held in solution and their industrial importance may be considerable.

The Dissolved Solids—The dissolved solids usually determined are shown in Table 4, which gives also the combining weights and reaction coefficients of the several radicals. Number of parts per million multiplied by the reaction coefficient will give milli equivalent weights.

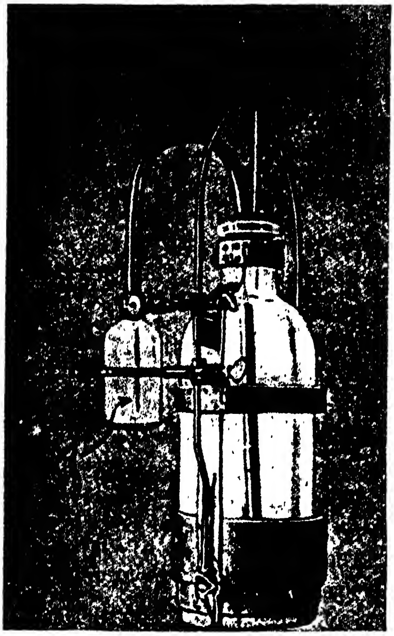

Fig. 8. Sampling Device when Dissolved Gas Must be Determined.

The alkali radicals are frequently estimated and reported as sodium, the separation of the other radicals of the group being omitted. Since sodium is nearly always 75 per cent or more of the group, and the several members have similar significance, this practice will lead to no serious error for most industrial purposes. Calcium and magnesium are the only members of the alkaline-earth group ordinarily determined; the others, where present, being found in relatively insignificant proportion. Manganese, iron, and aluminum are often determined together as oxides and so reported. Acidity is reported in terms of hydrochloric acid, sulfuric acid, or calcium carbonate. Chloride and sulfate radicals are usually determined, but other strong-acid radicals, which are rarely in sufficient proportion to be of great industrial importance, are generally omitted in untreated water. The weak-acid radicals may be determined together by the "alkalinity" titration, although separate determination of free carbon dioxide (CO_2), half-bound carbon dioxide (HCO_3), and fully bound carbon dioxide (CO_3) are often made. When the other weak-acid radicals are absent, or nearly so, as is usually the case, such analyses are satisfactory. A determination of total solids is also frequently made and serves as a check on the sum of solid constituents computed from the individual analyses.

There are a number of so-called industrial methods of analysis, giving directly such qualities of water as total hardness, temporary hardness, and incrustants. These are useful approximations, but they will not be given further consideration here because the complete mineral analysis gives more definitely the information afforded by such tests, as well as much valuable information that they cannot supply.

EXPRESSION OF RESULTS

The quantities of constituents found in water analysis have, in past, been reported by several different systems, but best modern usage favors expression in terms of milligrams of constituent per liter of water.

This is essentially a statement in parts per million by weight for waters sufficiently pure to be used for industrial purposes, and is often so reported. Conversion to this from other forms that have been extensively used can be made by use of the following factors:

From parts per hundred thousand, multiply by	10.0
From grains per imperial gallon, multiply by	14.3
From grains per U. S. gallon, multiply by	17.1
From pounds per 1000 U. S. gallons, multiply by	120.0

The constituents were at one time reported as acid and basic anhydrides, as is still the custom in mineral analysis, but the present day preferred practice is to report all constituents as milligrams of positive and negative radicals, or better still, to report reacting units computed by dividing milligrams of radical by combining weight of the radical, or by multiplying by the corresponding reaction coefficient. On this basis, the equivalent quantities of acid and basic constituents are made apparent at once and the so-called hypothetical combinations may be readily computed if desired. Estimations of hypothetical combinations which were formerly popular, are of doubtful value, beyond giving an approximation of the composition of solid compounds which would be deposited in the event of evaporation to dryness.

TABLE 4—CONSTITUENTS USUALLY DETERMINED IN MINERAL WATER ANALYSIS

Basic Radicals	*Combining Weights*	*Reaction Coefficient* *	*Acid Radicals*	*Combining Weights*	*Reaction Coefficient*
Alkali:			Strong-acid:		
Sodium (Na)	23.0	0.0435	Nitrate (NO_3)	62.0	0.0161
Potassium (K)	39.1	0.0256	Chloride (Cl)	35.5	0.0282
			Sulfate (SO_4)	48.0	0.0208
Alkaline-earth:					
Calcium (Ca)	20.0	0.0499	Weak-acid and hydroxide:		
Magnesium (Mg)	12.2	0.0822			
			Sulfide (S)	16.0	0.0624
Hydrogen and weak-base:			Bisulfide (HS)	33.1	0.0302
			Carbonate (CO_3)	30.0	0.0333
Hydrogen (H)	1.0	0.9921	Bicarbonate (HCO_3)	61.0	0.0164
Aluminum (Al)	9.0	0.1107	Hydroxide (OH)	17.0	0.0588
Manganese (Mn)	27.5	0.0364			
Iron (Fe), ferric	18.6	0.0537	Silica (SiO_2)	60.1	
Iron (Fe), ferrous	27.9	0.0358	(Probably colloidal)	(mol. wt.)	

* Reaction coefficient is the reciprocal of combining weight.

The relationship of the various methods of computation is shown in the tabulated report on a sample of a certain ground water in Table 5:

The acid and basic components should be equivalent and it will be noted that they are so within the limits of analytical error in this illustration.

Such a report is susceptible of as complete an interpretation as if hypothetical combinations are reported, but if these are desired, they may be computed on the assumption that the least soluble compound will appear first and the most soluble last. This will give an additional report as shown in Table 6:

TABLE 5—METHOD OF REPORTING A TYPICAL ANALYSIS

Component	*Grain per U. S. Gallon*	*Pounds per 1000 Gal.*	*Milligrams per Liter*	*Reacting Units per Liter*
Silica (SiO_2)	0.293	0.0417	5.01	....
Iron, aluminum and manganese oxide (Fe_2O_3)	0.207	0.0294	3.53	....
Sum of colloidal	0.500	0.0711	8.54	....
Sodium (Na)	0.351	0.0501	6.02	0.262
Potassium (K)	0.307	0.0438	5.26	0.134
Calcium (Ca)	4.405	0.628	75.41	3.762
Magnesium (Mg)	1.413	0.217	24.19	1.990
Sum of basic	6.476	0.9389	110.88	6.148
Chloride (Cl)	0.264	0.0376	4.52	0.127
Nitrate (NO_3)	0.020	0.0028	0.34	0.005
Sulfate (SO_4)	1.923	0.274	32.91	0.685
Carbonate (CO_3)	9.365	1.335	160.21	5.335
Sum of acid	11.572	1.6494	197.98	6.152

INTERPRETATION OF RESULTS

Each constituent impurity has its distinctive effects on the industrial value of a water and these may, therefore be considered individually, together with the specific methods of removal.

Suspended Matter—Suspended matter is harmful in most industrial processes. It is visible, however, and therefore the effects are readily observed, and the degree of purification obtained by any method of treatment is easily seen. Suspended matter may usually be considered chemically inert, and its effects are essentially the mechanical effects of ordinary dirt. Mechanical interference with such processes as dyeing, bleaching, and scouring, and discoloration of the products of manufacture are chief industrial effects of using turbid water. The methods used for purifying water with respect to other substances are usually effective in removing suspended matter, so that no special treatment is required except when other purification is unnecessary. City water supplies are often treated primarily to clarify them. Filtration preceded by coagulation is effective, though sedimentation alone may sometimes be used to remove all but the finest particles.

Colloidal Matter—Colloidal matter, like suspended matter, is chemically inactive. Alumina is too little in quantity and too innocuous to warrant treatment. Iron oxide may precipitate and leave the characteristic reddish-yellow stain. Silica, which is a relatively important constituent of soft waters of low concentration, is not particularly deleterious, though it is likely to precipitate. It slowly forms a hard porcelain-like scale on tubes of boilers operated at high pressure and may thus cause serious trouble. No special methods for the removal of silica have been developed. It is decreased, however, by filtration, water softening, and most other methods of treatment, and especially by use of sodium aluminate.

TABLE 6—METHOD OF COMPUTING HYPOTHETICAL COMBINATIONS

Compound	*Formula*	*Reacting Units per Liter*	*Reacting Weight*	*Milligrams per Liter*	*Grains per U.S. Gallon*	*Pounds per 1000 Gallons*
Silica	SiO_2	....	....	5.01	0.293	0.0417
Iron and aluminum	Fe_2O_3	....	....	3.53	0.207	0.0293
Magnesium carbonate	$MgCO_3$	1.990	42.16	83.95	4.915	0.700
Calcium:						
Carbonate	$CaCO_3$	3.345	50.03	167.40	9.790	1.395
Sulfate	$CaSO_4$	0.417	68.06	28.40	1.660	0.237
Sodium sulfate	Na_2SO_4	0.262	71.03	18.65	1.090	0.155
Potassium:						
Sulfate	K_2SO_4	0.006	87.13	0.52	0.030	0.004
Nitrate	KNO_3	0.005	101.10	0.51	0.030	0.004
Chloride	KCl	0.123	74.55	9.20	0.535	0.077
Total		6.148	....	317.17	18.550	2.643

Dissolved Carbon Dioxide—Dissolved carbon dioxide is present in practically all waters, being low in streams and very high in some ground waters. This substance is an agent in corrosion of well casings, pipes, boilers, etc. It is removed by heating or by treatment with caustic lime or other suitable chemical. Hydrogen sulfide, even in small quantity, is easily detected by its characteristic odor of rotten eggs. It occurs in badly polluted streams and in many ground waters, though probably only a small per cent of the well waters in the United States contain it. Like carbon dioxide it is an aid to corrosion. Because it forms dark-colored precipitates with many chemicals, it is deleterious in many industrial processes. Aeration or treatment by heating effectively removes it. Oxygen is in solution in practically all waters. It can be removed by heating. It is an agent in corrosion but is otherwise generally innocuous.

Sodium and Potassium—Sodium and potassium are constituents of nearly all rocks and are present in all natural waters. The content of sodium is increased by several systems of water treatment. Potassium rarely has more than a fourth to a third the concentration of sodium. The compounds of these alkalies are readily soluble and are, therefore, relatively important constituents of all highly concentrated waters. Fortunately, they are detrimental in but few industrial processes. Concentration in boilers leads to foaming, and dilution must be accomplished by "blowing off" the excess of concentrated water and replacing it with fresh. This, of course, results in material loss of heat. Concentration of sugar waters in refining sugar tends to produce liquors high in content of alkalies. If the proportion of alkalies to sugar is great, interference with crystallization and waste of sugar by retention in the mother liquor result. Distillation is the only practical method of purifying water with respect to sodium and potassium.

Calcium and Magnesium—Calcium and magnesium radicals are among those most widely distributed in nature. They are present in greater or less proportion in nearly all natural waters, giving to them the property defined as hardness, which is so detrimental in many chemical industries. When water is boiled, calcium tends to precipitate as the carbonate or sulfate, and magnesium as the carbonate or hydrate. The tendency to precipitate on heating renders calcium and magnesium undesirable constituents of water for all industrial purposes in which water is heated or is used for cooling purposes. The industrial effects were discussed in detail in connection with the several industries. Removal is ordinarily accomplished by water-softening processes combined with settling or filtration.

Iron, Aluminum and Manganese—In general iron, aluminum, and manganese are undesirable constituents in industrial waters, chiefly because of the accompanying tendency to precipitation and corrosion. The constituents of this group are especially susceptible to reactions in which they are deposited by oxidation, or otherwise removed from the system. Many of their compounds are readily hydrolyzed and ionized in such a way as to impart an acid reaction to the solution. The deposited constituents, as well as acidity, are harmful in many industrial processes. This is particularly true of iron, which leaves dark stains that are very difficult to remove. In paper making, textile-manufacturing, and preparation of beverages ferruginous waters are especially undesirable. In general, water-softening processes are effective in removing constituents of this group. Aeration and filtration through sand, coke or artificial zeolites are important methods of removing iron and manganese.

Nitrate—Nitrate is seldom a prominent constituent of waters and is, in general, derived from the oxidation of organic matter. Nitrates are oxidizing agents and on this account are deleterious in many industrial processes, though on account of their relatively small concentration they may usually be ignored.

Chloride—Chloride is present in practically all waters, and, since the chlorides of bases found in water are very soluble, the chloride radical is a prominent constituent of nearly all highly concentrated waters. Chlorides in processes treating foodstuffs or beverages tend to give a salty taste and excessive amounts must therefore be avoided. They affect organic matter and hence interfere with tanning, malting, fermentation, and other processes dealing with organic matter. Chloride can be effectively removed only by distillation, or by the use of the organic zeolites which remove anions.[80]

[80] See p. 223.

Sulfate—Sulfate is most noteworthy in regions of sedimentary rock formation and is often directly traceable to deposits from sea water or to oxidation of sulfur and sulfides. Sulfate is usually associated with lime or magnesia and thus is an undesirable constituent of boiler water, though it may be advantageous in processes of tanning [31] and ale brewing.

TABLE 7—MILLIGRAMS PER LITER, BY WEIGHT

Radical	*Lake Superior, Sault Ste. Marie, Michigan*	*Deschutes River, Moody, Oregon*	*Mississippi River, New Orleans, Louisiana*	*Green River, Greenriver, Wyoming*	*Youghiogheny River, McKeesport, Pennsylvania*	*Bumpass Hot Springs, Shasta County, California*
Basic:						
Na	3.2	6.7	13.	32.	8.0	16.
K		1.6			1.8	14.
Ca	13.	5.1	32.	41.	23.	8.9
Mg	3.1	1.6	8.4	13.	6.7	5.1
Fe	.06	.04	.5	....	4.7	1.4
Al	....	....	....	....	....	5.3
H	....	....	....	....	.5	.37
Total	19.36	15.04	53.9	86.	44.7	51.1
Acid:						
NO_3	.50	.22	2.5	.12	1.1	trace
Cl	1.1	1.2	9.7	15.	4.5	trace
SO_4	2.1	3.6	24.	81.	123.	141.
HCO_3	56.	34.	111.	140.	0.0	0.0
Total	50.70	39.02	147.2	236.12	128.6	141.
Grand Total	79.1	54.1	201.1	322.1	173.3	192.1

MILLIGRAM REACTING UNITS PER LITER

Basic:						
Na	.14	.29	.57	1.39	.35	.70
K		.04			.05	.36
Ca	.65	.25	1.60	2.04	1.15	.44
Mg	.25	.13	.69	1.07	.55	.42
Fe	.00	.00	.02	....	.17	.05
Al	....	....	....	....	....	.59
H	....	....	....	....	.50	.37
Total	1.04	0.71	2.88	4.46	2.77	2.93
Acid:						
NO_3	.01	.00	.04	.00	.02	trace
Cl	.03	.03	.27	.42	.13	trace
SO_4	.04	.08	.50	1.69	2.56	2.93
HCO_3	.92	.56	1.82	2.29	.00	.00
Total	1.00	0.67	2.63	4.40	2.71	2.93
Grand Total	2.04	1.38	5.51	8.90	5.48	5.86

The lime soda process largely, and the zeolite process completely, changes the sulfates of the alkaline earths to sodium sulfate, which is usually harmless, although it remains in solution. For actual removal of the sulfate radical, pre-

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[31] See Chapter 45.

cipitation with barium carbonate or hydrate is effective, but expensive and inadmissible in potable water supplies. Distillation may be resorted to as an extreme remedy.

Carbonate and Bicarbonate—Carbonate and bicarbonate can be reduced in hard waters by heating or by the lime soda process of water softening. Carbonates in irrigation water are sometimes corrected by the use of gypsum or land plaster. In most industrial waters the bicarbonate is the dominant acid radical and in moderate concentration is harmful in but few processes. In steam making it is precipitated as a soft scale when calcium or magnesium is present. Other weak-acid radicals are not of great industrial importance.

The Total Solids—The total solids or sum of all constituents, when considered together with the individual character of the impurities, will indicate the quality of a water for industrial purposes. Natural waters are found ranging from one extreme to the other in content of all the various constituents, but industrially valuable waters are usually of relatively low total solid content. Analyses of typical industrially useful waters showing reacting values and character formulae are reported in Table 7.

SUMMARY

The subject of water supply is introduced by a brief historical sketch showing its development from ancient beginnings, and the magnitude of the present-day industry. The sources and nature of water supply are discussed showing the type of impurities present in rain water, surface water, and ground waters. The requirements of specialized industries are reviewed, including the needs for municipal, chemical, steam-making, etc. The methods of examination of water are outlined, taking up methods of sampling, sanitary analysis and mineral analysis and outlining systems of expressing results and the effects of the various impurities such as turbidity, organic contamination and the several dissolved solids.

Water purification systems are discussed, including methods for removal of volatile impurities by aeration, suspended impurities by settling, coagulation, slow or rapid sand filtration, removal of organic contamination by copper, chlorine, or ultra-violet light, removal of soluble matter by pre-heating, lime soda or zeolite treatment or by distillation.

Methods for the examination of water supply expression and interpretation of results and a Reading List are appended.

READING LIST

EXAMINATION AND ANALYSIS

American Public Health Assoc., "Standard Methods for Examination of Water and Sewage," eighth edition (1936).
Dorsey, N. E., "Properties of Water" (1939).
Mason, W. P., "Examination of Water," sixth edition (1931).
Parr, S. W., "Examination of Fuel, Gas and Water," fourth edition (1932).
Prescott and Winslow, "Elements of Water Bacteriology," fifth edition (1931).
Whipple, G. C., "The Microscopy of Drinking Water," fourth edition (1927).

WATER PURIFICATION

American Water Works Assoc., "Water Works Practice," fourth edition (1939).
Buswell, A. M., "Chemistry of Water and Sewage Treatment," second edition, A. C. S. Monograph, Reinhold Publishing Corp., in prep. (1942).

Ellms, J. W., "Water Purification," second edition (1928).
Flinn, Weston and Bogert, "Water Works Handbook," third edition (1927).
Folwell, A. P., "Water Supply Engineering," second edition (1911).
Hall, R. E., "Physico-chemical Study of Scale Formation and Boiler Water Conditioning" (1926). Also later journal articles.
Hopkins, E. S., "Water Purification Control," second edition (1936).
Jackson, P. G., "Boiler Feed Water," third edition (1922).
Mason, W. P., "Water Supply" (1916).
Parsons, W. H., "Water Works Administration" (1926).
Paul, J. H., "Boiler Chemistry and Feed Water Supply," second edition (1923).
Powell, S. T., "Boiler Feed-water Purification," new edition (1939).
Rideal and Rideal, "Water Supplies, Their Purification, Filtration and Sterilization" (1914).
Ryan, W. J., "Water Treatment and Purification" (1937).
Stein, M. F., "Water Purification Plants and Operation," fourth edition (1939).
Turneaure and Russel, "Public Water Supply," third edition (1924).
Wolman, A., "Manual of American Water Works Practice" (1939).

BOILER WATER TREATMENT

"Boiler House and Power Station Chemistry," E. Arnold & Co., London (1940).

SECTION II

HEAVY CHEMICALS AND ALLIED PRODUCTS

The *Heavy Chemicals* might be considered to be those that are produced in large quantities—usually at low cost. They usually serve as raw materials or treating agents for other process industries.

CHAPTER 7

SULFURIC ACID

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PROCESSES OF MANUFACTURE

Sulfuric acid was one of the first acids isolated. It was known to the Arabians in the eighth century and to Europe in the fourteenth and fifteenth centuries, when chemical industries really began to develop. The old name, "oil of vitriol," is derived from its first preparation by the alchemists Geber, Valentine, and their predecessors, who made it by distillation of green vitriol ($FeSO_4$) and similar sulfates. They also obtained it by the burning of sulfur mixed with saltpeter. It is now made by either of two methods, the "chamber" process (sometimes called "nitration" process) and the more modern "contact" process, for both of which the usual raw material is sulfur or sulfides, which are burned to SO_2 with excess of air. The SO_2 is then caused to combine with oxygen and water to form H_2SO_4, the two methods differing as described below.

In the chamber process the gases from the burner are mixed with oxides of nitrogen (so-called "niter") and water in large leaden chambers. A diluted sulfuric acid containing "niter" is formed; this is passed through a so-called "Glover" tower counter-current to the hot burner gases which thus remove the "niter" and concentrate the acid to 75 to 80% (58° to 61° Baumé). If stronger acid is desired, it must be made by a separate concentrating process. Another tower, the "Gay-Lussac," recovers the oxides of nitrogen from the waste gases by washing them with strong acid.

The contact process passes the dry burner gases through a closed tank called a "converter," containing a granular catalyst, where SO_3 is formed by oxidation in the gas phase. The SO_3 is then absorbed in sulfuric acid, to which water is also added. In this way acid of any desired strength may be made, even acid containing excess of SO_3, called "fuming acid" or "oleum."

Forms of Occurrence—Sulfuric acid is found in commerce in many different strengths. Those customarily used as standard in the United States are designated in Table 1:

The term "20% Oleum" means 20 parts SO_3, 80 parts H_2SO_4. The figure "104.49% H_2SO_4" signifies that if 100 lbs. of the oleum are diluted with water so as to make monohydrate, 104.49 lbs. of monohydrate will be obtained.

In selling acid, the actual weight is calculated to some one of the above standards. Statistics of national production are calculated to 50° Bé. (62.2%)

acid. Factory accounts of sulfuric acid manufacturers using the chamber process are usually calculated to 50° Bé. (62.2%) acid, or sometimes 60° Bé. (77.7%) acid; those using the contact process are calculated to monohydrate.

TABLE 1—COMMERCIAL STRENGTHS OF SULFURIC ACID

Chamber acid	50° Bé.,	62.18% H_2SO_4
Glover acid, or Tower acid	60° Bé.,	77.67% H_2SO_4
Oil of vitriol ("O. V.")	66° Bé.,	93.19% H_2SO_4
Monohydrate		100.00% H_2SO_4
Fuming acid, or 20% oleum (20 parts SO_3, 80 parts H_2SO_4)		104.49% H_2SO_4
40% oleum		109.00% H_2SO_4

Chamber acid, as actually made, may be 50° to 55° Bé. (62.2% to 69.7%), Glover acid may be 58° to 63° Bé. (74.4% to 83.3%) and O. V. may be 65.5° to 66° Bé. (90.6% to 93.2%).

PROPERTIES OF SULFURIC ACID

Strong sulfuric acid is a heavy, oily liquid, practically colorless, odorless when pure, but sometimes smelling of SO_2 which is generally present in excess when the acid is formed. Boiling points of various strengths at atmospheric pressure and at various vacua are charted in Figure 1. Weak acid boils with evolution of practically pure water; as the concentration increases, H_2SO_4 appears in the vapor in increasing proportions, reaching 1% by weight when the liquid contains 75 to 85%. The constant-boiling mixture is reached at 98.3% (337° C.), the evolved vapor having the same percentage composition as the liquid. Stronger acids on boiling are eventually reduced to 98.3%. The vapor evolved from these strong acids partly dissociates into a mixture of SO_3, SO_2, O_2, and H_2O. The degree of dissociation is a function of the temperature; e.g., acid of 99.62% H_2SO_4 boiled in partial vacuum shows negligible dissociation below 230° C., but at 250° C., 9% of the vapor is dissociated.[1] Further

TABLE 2—WEIGHT CONVERSION FACTORS FOR COMMERCIAL STRENGTHS OF SULFURIC ACID

	50° Bé.	*60° Bé.*	*66° Bé.*	*Monohydrate*	*20% Oleum*	*40% Oleum*	*60% Oleum*
50° Bé.	......	0.8006	0.6672	0.6218	0.5951	0.5705	0.5478
60° Bé.	1.2491	......	0.8335	0.7767	0.7433	0.7126	0.6843
66° Bé.	1.4987	1.1998	......	0.9319	0.8919	0.8550	0.8211
Monohydrate	1.6082	1.2875	1.0731	......	0.9570	0.9174	0.8811
20% Oleum	1.6804	1.3453	1.1213	1.0449	......	0.9586	0.9206
40% Oleum	1.7530	1.4034	1.1697	1.0900	1.0432	......	0.9604
60% Oleum	1.8253	1.4613	1.2179	1.1350	1.0862	1.0413	......

Based on tables of Manufacturing Chemists' Association of the United States; see book of tables entitled "Chemical Plant Control Data," pub. Chemical Construction Co. (1935).

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[1] Thomas, J. S., and Ramsay, J. Chem. Soc., *123*, 3265 (1923).

data on boiling points will be given (Table 6) later in this chapter, under the heading "Concentrating Sulfuric Acid."

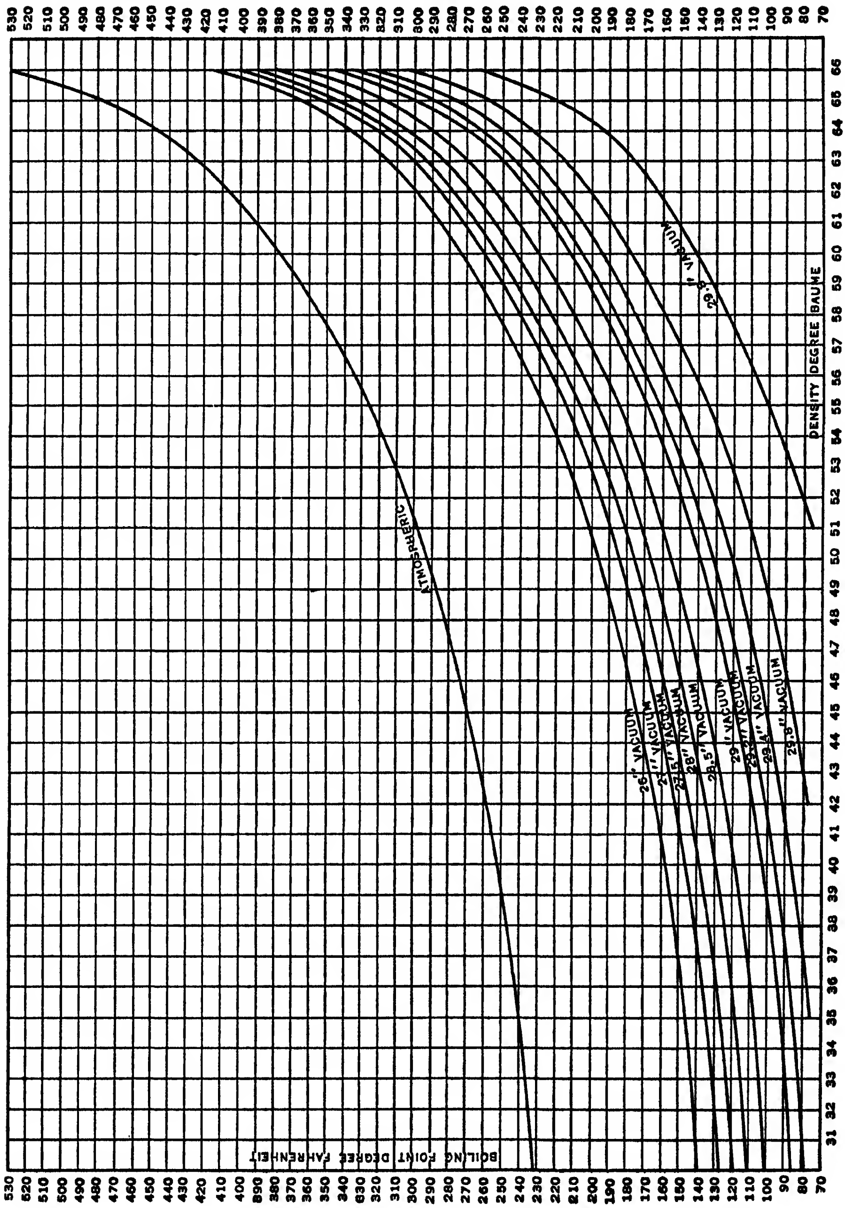

Fig. 1. Boiling Point of Sulfuric Acid.

The specific gravity (at 60° F. compared with water at 60° F.) increases with strength up to 1.8437 for 97% H_2SO_4, then decreases to 1.8391 for 100% H_2SO_4, then increases to 2.10 for 60% oleum (60 parts SO_3, 40 parts H_2SO_4), then decreases to 1.857 for 100% oleum (pure SO_3). The gravity (usually measured in deg. Bé.) is a reliable indication of the strength of the acid only up to about 66° Bé. (93.19% H_2SO_4).

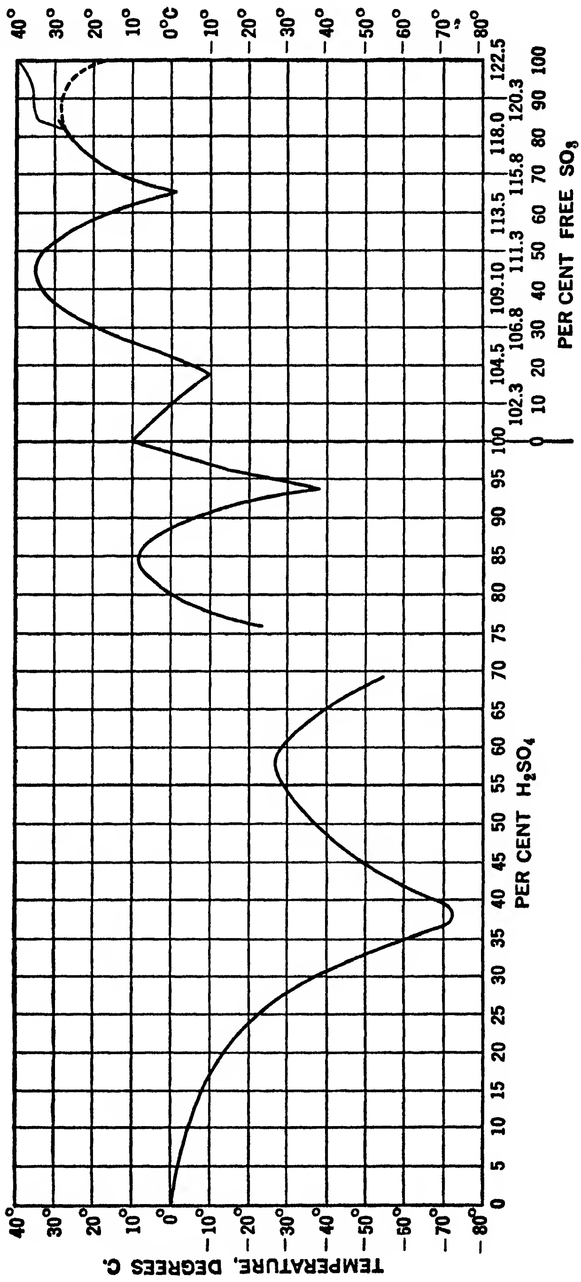

FIG. 2.

The variations in freezing point with strength of acid are great and irregular. Figure 2 shows the freezing points of acid of 0 to 100% H_2SO_4 and of oleum of 0 to 100% free SO_3. The dotted line beyond 80% oleum is for freshly made acid; on standing it polymerizes, approaching the values given by the solid line.[2] The irregularities in the freezing-point curve and in the specific gravity are due to the existence of definite hydrates[2a] of H_2SO_4.

TABLE 3—CORROSION OF MATERIALS BY H_2SO_4

Metals	*Dilute H_2SO_4*		*Strong H_2SO_4*	
	Cold	*Hot*	*Cold*	*Hot*
Platinum	nil	nil	nil	very slight
High-silicon cast iron with 13 to 15% silicon	nil	nil	nil	very slight
Lead	very slight	slight	slow < 95%	slow < 80%
Monel metal	very slight *	slowly attacked	very slight < 85% *	attacked
Stainless steel 18% Cr; 8% Ni	resistant * attacked †	attacked	resistant * attacked †	attacked
Stainless steel high Ni content	resistant	fairly resistant	resistant	fairly resistant
Iron or steel	attacked < 65%	attacked < 93% or > 50° C.	safe > 75%	slow > 93%
Non-Metals				
Silica	nil	nil	nil	nil
Sulfur	nil	nil	nil	slowly attacked
Rubber	resists < 50%	resists < 50% if < 85° C.	attacked > 50%	attacked > 50% or > 85° C.
Concrete, brick, masonry containing basic constituents	bad	bad	bad	bad
Paints, varnishes, enamels, and lacquers	some withstand	practically all attacked		

NOTE: The designation "nil" indicates absence of noticeable attack, or a loss of weight of less than 1 mg. per sq. dm. per day.

* If the acid contains dissolved air.

† Air-free acid.

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[2] Fairlie, A. M., "Sulfuric Acid Manufacture," Reinhold Publishing Corp., New York, 1936, p. 470.

[2a] Pickering, S. U., J. Chem. Soc., *57*, 331-369 (1890).

The specific heat of H_2SO_4 is 0.33.

Strong acid and oleum have a powerful dehydrating action, breaking down animal tissue and skin and many other organic materials by robbing them of water, and in some cases carbonizing and blackening them. Severe burns produced by sulfuric acid are best treated by the instant application of large quantities of water. Unless large quantities are available, first wipe away the acid with something dry before washing, as the heat of dilution with small quantities of water or with alkali is very great, and would accentuate the burn. Then treat with a sterilized emulsion of sweet oil and lime water or ammonium carbonate. For the eyes, bicarbonate of soda should be used instead of the stronger alkalies.

Materials of Construction—The metals now customarily used to handle cold sulfuric acid are: lead or stainless steel for strengths up to 95%, steel or iron for strengths over 75%. For hot acid, lead is safe only up to 80%, and steel and iron can be used only above 93%, and then only in the absence of agitation which washes off the protective coating of sulfate. Therefore for hot acid between 80% and 93%, cast irons containing 14% silicon ("Duriron," "Corrosiron," "Tantiron," etc.) are used, or, if greater tensile strength is required, high-nickel alloys such as "Hastelloy D." Ceramics and acidic brick are used for all strengths and temperatures. Table 3 and Appendix "A" to this chapter give more detailed information on the corrosion-resistance of various materials.

ECONOMIC ASPECTS

The magnitude of the yearly production of sulfuric acid in the United States is perhaps not generally appreciated. Its tonnage in normal years is three to four times that of soda or one and a quarter times that of white sugar; in 1940 it was one-ninth that of gasoline. In spite of the recent extensive changes in products and processes in the chemical and allied industries, the demand for sulfuric acid has not appreciably decreased. New processes are supplanting some of the old-established uses of sulfuric acid, but other new uses spring up. In 1940, consumption in the United States surpassed that of the previous all-time peak reached in 1937.

Furthermore, the low cost of sulfuric acid made under favorable circumstances, and the very large investment in plant for its manufacture and use, tend to prevent any sudden or radical change in the economic status of this very important material.

Both production and consumption of sulfuric acid are widely distributed throughout the United States. The cost of transportation, even in steel tank-cars, being high in proportion to the value of the product, encourages the building of acid plants at or near the point of consumption. Table 4 gives a list of production and consumption by states as of 1929 (later data on product is not available) and distribution of plants in 1929 and 1937. The trend toward larger plants is seen in the decrease of number from 288 in 1929 to 183 in 1937, while the total consumption increased slightly as shown by Table 5.

Uses and Production by Grades—The principal uses of sulfuric acid, and their trends in recent years, are shown in Table 5.

TABLE 4—SULFURIC ACID PLANTS, PRODUCTION AND CONSUMPTION BY STATES, 1929. CHAMBER AND CONTACT PLANTS BY STATES, 1929 AND 1937.

State	*Per Cent Production in 1929*	*Per Cent Consumption in 1929*	*Plants in 1929*		*Plants in 1937*		
			Chamber	*Contact*	*Chamber*	*Contact*	*Both*
Alabama	2.35	3.66	14	1	7	2	..
Arizona	†	0.22	1	1	1	1	..
Arkansas	0.51	0.10	4	1	..	..	..
California	4.70	4.55	6	6	..	7	1
Colorado	0.51	0.48	1	2	..	2	..
Connecticut	†	3.05	2	......	1	..	1
Delaware	†	0.12	......	1	..	..	..
Florida	0.86	1.52	5	1	3	1	..
Georgia	3.34	4.87	32	......	18	..	..
Illinois	8.20	5.71	13	4	7	6	..
Indiana	1.89	4.73	2	2	..	2	1
Iowa	†	0.11	......	......	..	..	..
Kansas	†	1.00	1	......	..	..	..
Kentucky	†	0.28	......	1	..	1	..
Louisiana	1.26	2.09	6	3	3	2	..
Maine	....	0.15	......	......	..	..	..
Maryland	8.70	6.39	10	3	5	2	1
Massachusetts	3.53	2.32	6	2	1	1	..
Michigan	0.88	2.59	2	2	2	1	..
Minnesota	0.76	0.30	7	......	..	..	..
Mississippi	†	0.57	......	1	4	..	..
Missouri	†	0.98	......	1	..	2	..
Montana	†	0.05	1	......	1	1	..
Nebraska	....	0.06	......	......	..	..	..
New Hampshire	....	0.13	......	......	..	..	..
New Jersey	11.98	8.34	15	8	4	4	2
New Mexico	....	0.04	......	......	..	..	..
New York	2.27	7.29	5	2	1	1	1
North Carolina	2.39	3.31	17	......	9	..	..
Ohio	7.20	8.43	16	3	10	2	1
Oklahoma	1.02	0.07	1	2	..	2	..
Oregon	....	0.01	......	......	..	..	..
Pennsylvania	11.70	10.79	17	8	6	9	2
Rhode Island	....	0.34	......	......	..	1	..
South Carolina	2.15	2.92	13	......	10	..	..
Tennessee	7.83	1.20	8	1	6	..	1
Texas	3.91	4.56	3	5	1	5	..
Utah	†	0.10	1	1	..	2	..
Vermont	....	0.08	......	......	..	..	..
Virginia	2.90	3.51	8	1	6	3	..
Washington	†	0.19	1	1	..	1	..
West Virginia	†	1.31	2	......	1	1	..
Wisconsin	0.25	0.75	1	3	..	2	..
Wyoming	....	0.73	......	......	..	1	..
Undistributed	8.91	....	......	......	..	..	..
Totals	100.00	100.00	221	67	107	65	11

† Production percentages for states having two or less plants are lumped in the undistributed total.
1929 Statistics from Chem. and Met. Eng., Jan., 1930, p. 4.
1937 Statistics from Minerals Yearbook, 1938, Bur. Mines.

The Shifting Demand—In the last few decades, the uses of sulfuric acid in the United States have changed considerably. Early in the century about half of the sulfuric acid produced was used in the manufacture of fertilizers and the remainder in the manufacture of explosives, oil-refining, pickling of steel plate, and the preparation of heavy chemicals. For most of these purposes, the acids made by the chamber plants (50° to 60° Bé., i.e., 62% to 78%) were of adequate strength. The stronger 66° Bé. (93.2%) acid was made, when required, by heat-concentration of chamber-plant acids, which added 20% to 50% to the cost of the acid (per unit of H_2SO_4 content). The comparatively small quantity of oleum required was produced in a few scattered contact plants, using platinum catalyst with none too satisfactory an efficiency. Pyrites ore was the usual source of the sulfur dioxide gases for both types of plants.

TABLE 5—CONSUMPTION OF SULFURIC ACID BY INDUSTRIES *

(Total Acid calculated to tons of 50° Bé.)

Consuming Industries	*1929 Boom*	*1932 Depression*	*1937*	*1939*	*1940*	*Per Cent 1940*
Fertilizers	2,418,000	780,000	2,510,000	1,970,000	2,260,000	24.70
Petroleum refining	1,570,000	1,240,000	1,210,000	1,210,000	1,270,000	13.88
Chemicals	890,000	674,000	1,020,000	975,000	1,090,000	11.91
Coal products	935,000	375,000	860,000	740,000	900,000	9.83
Iron and steel	800,000	270,000	850,000	980,000	1,200,000	13.12
Other metallurgical	675,000	310,000	620,000	570,000	640,000	6.99
Paints and pigments	225,000	160,000	525,000	520,000	570,000	6.23
Explosives	195,000	120,000	230,000	160,000	175,000	1.91
Rayon and cellulose film	150,000	176,000	380,000	405,000	470,000	5.14
Textiles	90,000	75,000	112,000	116,000	125,000	1.37
Miscellaneous	390,000	230,000	400,000	384,000	450,000	4.92
Totals	8,338,000	4,410,000	8,717,000	8,030,000	9,150,000	100.00

* Data from Chem. and Met. Eng., *38*, 35 (1931); *40*, 32 (1933); *45*, 83 (1938); *46*, 106 (1939); *48*, 91 (1941).

Rapid development of the explosives industry during the World War of 1914-18 caused an enormous increase in the demand for sulfuric acid of all strengths as shown in Figure 3. A great increase in chamber acid production was called for by the fertilizer industry, on account of European demands for American-grown cotton and foodstuffs. The increase in tower acid (60° Bé.) includes by-product acid from zinc and copper smelters. The preparation of "mixed acids" (nitric plus sulfuric) used in nitration processes of making high explosives required sulfuric acid, usually 20% to 40% oleum, as a direct constituent and 66° Bé. acid in the manufacture of the nitric acid.[8] This increase in demand compelled operation of all existing chamber plants in excess of their normal capacity, rapid building of concentrating plants for producing

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[8] For a discussion of the manufacture of nitric acid see Chapter 8.

66° Bé. (93.2%) acid from chamber acid (50° Bé., 62.2%) and tower acid (60° Bé., 77.7%), and for concentrating "nitration spent acids" for re-use, also a large increase in the number of contact plants. The concentrating of chamber-plant acid to 93%, if done as a separate operation, adds between 20% and 50% to the cost of the product (per unit of H_2SO_4), or somewhat less in processes utilizing the heat of the burners. However, since the contact plant can easily produce acid equivalent to 104.5% H_2SO_4 (i.e., 20% oleum) or by special design 108% H_2SO_4 (i.e., 35% oleum), and at a cost little if any greater per unit of H_2SO_4 than chamber-plant acid, obviously the cheapest method of strengthening the output of a chamber plant is by mixing it with contact acid, oleum, or even sulfur trioxide.[4] Many chamber plants had contact plants added for this purpose.

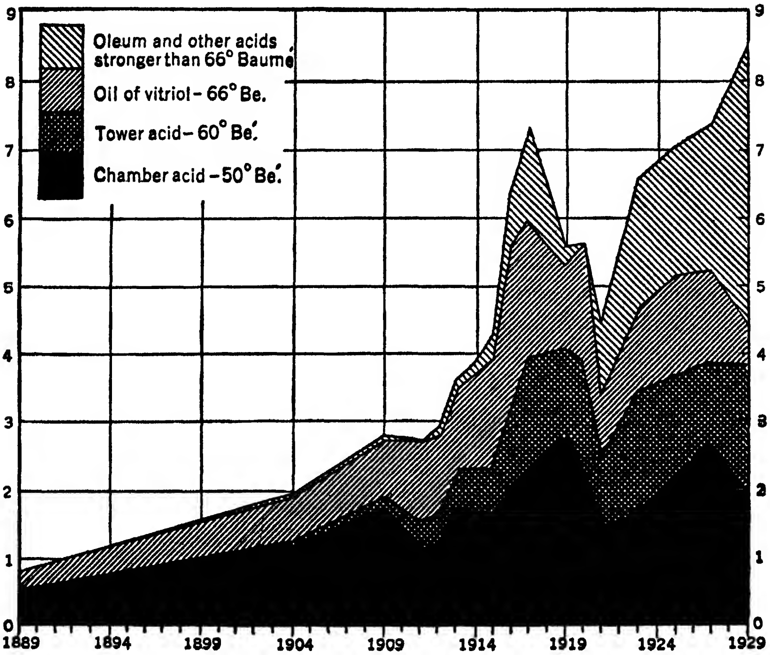

FIG. 3. Production of Sulfuric Acid by Strengths, 1889-1929 (million tons, 50° Bé. Basis). (Kreps, T. S., "The Economics of the Sulfuric Acid Industry," Stanford Univ. Press, 1938)

Sulfur became the principal raw material, due to its greater purity and consequent suitability for the contact process, to difficulty in importing pyrites, and to the development of efficient and simple sulfur furnaces.

After the War of 1914-18, the demand for the stronger acids declined rapidly until the growth of the dye industry brought a resumption of the demand for "mixed acids" and oleum. The fertilizer industry continued to use chamber-plant acid, but the depression in the fertilizer trade forced abandonment of many of those plants. However, the increase in the demand for

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[4] Gilchrist, Refiner, 9 (a), 85 (1930).

sulfuric acid from the rapidly expanding oil industry[5] required not only the manufacture of additional quantities of 98% acid and oleum, but the better recovery and concentration of the weak acid contained in the sludges produced by the treatment of oils with strong acid. At many oil refineries, equipment was installed to concentrate the sludge acid to 66° Bé. (as described later in this chapter), and in some cases contact acid plants were built at the refineries to produce strong acid for fortifying the sludge acid.

The result of these changing uses has been to increase the building of contact-process plants and restrict the building of chamber-process plants. (See discussion later, under the heading "Chamber Process vs. Contact Process.")

Certain Uses of Sulfuric Acid Diminishing. Among the possible processes in the chemical industry that would cause a decrease in the demand for sulfuric acid, the most important, if successful, would be the Dorr-Liljenroth processes for making ammonium phosphate fertilizer.[6] One of these processes uses no sulfuric acid at all, but is an electric-furnace process and hence requires very cheap electric power for its commercial success.

Another of the Dorr-Liljenroth processes utilizes gypsum, carbon dioxide, and ammonia, as does also the Merseburg process.

Some manufacturers have been using nitric acid instead of sulfuric in the manufacture of fertilizers. This idea was based on the supposed uselessness of the sulfate radical as a fertilizing agent. However, recent investigations indicate that sulfur in some form is a necessity in a "complete" fertilizer, i.e., a fertilizer that replenishes all the substances that plants remove from the soil.[7]

The petroleum industry, which has been the second largest consumer of sulfuric acid, is finding that for many purposes it is not necessary to employ acid treatment to the extent formerly considered necessary. Coupled with this fact is the growth of hydrogenation, in which any sulfur content of petroleum is transformed into H_2S, a potential raw material for sulfuric acid manufacture.

Various other fields for the use of sulfuric acid are also diminishing. Whereas some years ago all nitric acid, as well as all "niter-gas" used in sulfuric acid plants, was produced by treating Chile nitrate with sulfuric acid, now nearly all is derived from the oxidation of ammonia.[8] Such acids as acetic and formic are also being made without the use of sulfuric. Hydrochloric acid is also made directly from chlorine and hydrogen. Some coke plants are selling their ammonia as aqua o reven anhydrous ammonia instead of absorbing it in sulfuric acid. Phosphoric acid is in some cases used instead of sulfuric for fixing ammonia in fertilizers. Inhibitors and electro-chemical methods are reducing the quantity of sulfuric acid used in pickling iron and steel.

The foregoing examples illustrate that the demand for a product keeps changing with developments in other fields; that there is an interproduct

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[5] For a discussion of the use of sulfuric acid in the oil industry, see Chapter 14.

[6] For a discussion of fertilizers see Chapter 13.

[7] Fairlie, A. M., loc. cit., pp. 592-595.

[8] See Chapter 8.

competition that is always changing.[9] But, while sulfuric acid is being partially replaced in some fields, its use grows in others, for, as the data of Table 4 show, the use is at least holding its own, and perhaps increasing somewhat.

Cost of Manufacture—It is wise always to keep in mind the intrinsic commercial values of materials. No mistake of the young engineer is more fatal to his success than the loss of the practical man's confidence resulting from a proposal to "kill flies with a 16-inch gun" as one of them expressed it.

The rising and falling prices of materials and labor since the World War of 1914-18 have made estimates of manufacturing costs unreliable, except as applied to a given short period of time. Other factors causing uncertainty in published estimates are type and size of plant, allowance for interest and depreciation, allocation of overhead, marketing of acid versus consumption on the premises, etc. In old acid plants, the sodium nitrate used has been reported to cost $0.75 per ton of 60° Bé. acid[10]; this is now superseded by ammonia at about $0.25.[11]

However, as an indication for present day manufacturing costs it may be said that, based on 1937 costs in the United States, a modern brimstone plant with an efficient technical staff can produce a ton of 98% acid at a cost of $10.00, including interest on plant, amortization, repairs, power, labor and miscellaneous and "overhead charges." Of this, $7.00 is cost of sulfur and $3.00 is manufacturing cost. The purchaser would pay $13.50 per ton (in tank cars) and the manufacturer's profit would be about $1.50 on the sale.[12, 13, 14]

The manufacturing cost of 60° Bé. (77.7%) acid in a chamber plant, on the same basis, can be as low as $2.30. Adding a sulfur cost of $5.50 gives a total cost of $7.80, i.e., about the same per unit of H_2SO_4 content as the 98% contact acid.

In a plant making 98% acid from waste smelter gases the cost of manufacturing on the 1937 basis would be about $7.00. Of course this is the total cost, there being no expenditure for sulfur.

All the above costs are for large and efficient plants making about 100 tons a day; in small plants, or under unfavorable circumstances, as in old plants with high maintenance expense, they will be considerably higher. In the eastern part of the United States, as a rule the smallest economical size of plant, whether contact or chamber, is about 25 tons of H_2SO_4 per day.

In July, 1941, the quoted selling price was $16.50 for 98% acid in tank cars ($30.00 in carboys), $13.50 per ton for 60° Bé. acid (77.7%), and $18.50 per ton for 20% oleum.

Chamber Process vs. Contact Process—A. M. Fairlie[15] has well generalized the considerations leading to a choice between the various contact proc-

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[9] For further discussion of this point see Chapter 1.

[10] Tyler, Chem. and Met. Eng., *33*, 204-209 (1926).

[11] Fairlie, loc. cit., p. 583.

[12] Kreps, T. J., "The Economics of the Sulfuric Acid Industry," Stanford Univ. Press, 1938, pp. 72 and 118.

[13] Fairlie, loc. cit., pp. 572-573.

[14] Wells, A. E., and Fogg, D. E., U. S. Bureau of Mines Bulletin *184*, 124, 192 (1920).

[15] Fairlie, loc. cit., pp. 582-584.

esses and chamber processes. Without repeating the detailed statements made elsewhere in this chapter, we may summarize this as follows, remembering that local and economic conditions may modify the borderline cases.

1. If 98% acid or oleum are required, a contact plant must be used.
2. Oil of vitriol (66° Bé., 93.2%) can almost always be made more cheaply by diluting contact acid than by concentrating chamber acid.
3. The air-cooled lead-chamber is obsolescent, as are the Mannheim and the Tentelew platinum contact processes.
4. For 60° Bé. (77.7%) and weaker acids, the choice between liquid-cooled chambers, a vanadium contact plant, and a platinum contact plant is open; local conditions will decide each proposed installation. Much of the published data, of course, is written by persons financially interested in one certain angle of the matter.
5. The cost of catalyst, and hence the interest charges, varies greatly from time to time.
6. The chamber plant has greater flexibility in production-rate than the contact plant.
7. The contact plant has greater flexibility in the strength of the acid produced.
8. High-pressure chamber plants, e.g., 30 to 50 atmospheres, as suggested by E. Berl, are a future possibility, though offering great difficulties of design.

SOURCES OF RAW MATERIAL

The principal sources of sulfuric acid in order of magnitude are: (1) sulfur, (2) iron pyrites (FeS_2), (3) smelter gases or other waste gases containing SO_2, (4) gypsum (in Germany and France), (5) waste products from various industries.

In the United States until 1880, sulfur was used exclusively.[16] Due to a shift in relative costs, the use of pyrite then grew until in 1914 only 2.5% of the acid was made from sulfur. Then, the World War interfered with the importation of pyrite, and the success in the U. S. A. of the Frasch process for mining sulfur brought sulfur back into wide use. Since then, the development of improved sulfur-using contact-acid plants has aided the trend. In 1940,[17] 66% of the acid was made from sulfur, 22% from pyrite (of which 45% was imported), 11% from waste gases from zinc and copper ores, and a small quantity from H_2S at oil refineries. These figures do not include reclaimed acid from oil sludges, etc.

In other countries whose mineral resources are different, sulfur is not so dominant. For instance, Germany, in 1928, produced 90% of her acid from pyrites and zinc blendes.[18]

Sulfur—Crude sulfur, commonly called "brimstone," has come from two principal sources: volcanic deposits of Sicily and Japan and underground beds in Louisiana and Texas. So great has been the development of these latter that imports into the United States have ceased. In Louisiana and Texas,

[16] Kreps, loc. cit., p. 77.
[17] Chem. and Met. Eng., *48*, 91 (1941).
[18] Kreps, loc. cit., p. 105.

sulfur occurs chiefly mixed with limestone, both supposed to be the products of the reduction of calcium sulfate by carbonaceous matter and heat. There are numerous scarcely-developed deposits of this nature in the United States. The Louisiana deposits are mined in an ingenious way developed by Frasch. Holes are drilled down to the deposit and lined with an iron casing. Inside this casing are two pipes, one inside the other. Superheated water under pressure is forced down between the casing and the middle pipe, melting the sulfur in the ground. When sufficient molten sulfur has accumulated, compressed air is turned into the inner pipe, and the sulfur is "air-lifted" in the space between the inner and middle pipes.[19] In Texas, which now produces about 85% of the total, the procedure is similar.

The purity of the sulfur produced in the United States is very high, usually over 99.5% and sometimes 99.9%. In 1941, this sulfur sold for $16.00 per long ton, f.o.b. Gulf ports.

In Sicily, sulfur is mined from open pits and separated from the gangue by fusion and distillation.[20] It comes to the market as dirty yellow lumps of irregular shape and size.

A pure sulfur is made from pyrites by the "Orkla" process,[21] of which two installations have been made in Norway. The pyrite is smelted in a blast furnace with quartz, limestone and coke. The gases, containing sulfur, SO_2 and CS_2, are then catalyzed to CO_2 and sulfur.

Sulfur as such is recovered from smelter waste gases by the Consolidated Mining & Smelting Co. at Trail, British Columbia.

Pyrites—Pyrites, FeS_2, often carrying more or less copper sulfide, were first used in Europe about 1830, but in the United States not until about 1880. Of the total consumption, 45% is imported, chiefly from Spain, Portugal, and Newfoundland.

Prices are generally made per "unit," which is 1% of a short ton of sulfur content. Pyrites containing 45% sulfur, quoted at $.13 per unit, will thus cost $45 \times \$.13$ or $5.85 per short ton. The quotations in 1940 were $.12 to $.13 per unit, c.i.f. Atlantic ports.

In the United States, deposits have been developed in New York, New Jersey, and several of the southern Appalachian and Far Western States. Most of them are not as high grade as the imported ore, but a few others are of the finest character.

As impurities, copper, zinc, calcium, magnesium, and sometimes lead, are objectionable from the point of view of the acid maker, as they retain sulfur which oxidizes to sulfate and is not available for burning.

Arsenic, lead, and zinc are also harmful, for they volatilize and enter the process. In a "chamber" acid-making plant, arsenic in the pyrites used will in part appear in the finished acid, limiting its marketability. In a "contact" plant, if the catalyst is platinum on asbestos or on magnesium sulfate, it would be seriously "poisoned" unless the gas were thoroughly scrubbed free of arsenic.

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[19] For discussion of an analogous procedure in the mining of salt see Chapter 9.

[20] U. S. Bur. of Mines, Mineral Industries, Vol. 8, p. 592.

[21] Fairlie, loc. cit., p. 82.

"Coal brasses," another form of pyrite occurring as an impurity in coal, are now being separated in a condition suitable for making sulfuric acid.[22]

Waste Gases—The third source of sulfur is waste gases containing SO_2, particularly the "fumes" from sulfide smelters. These gases are otherwise worthless and in many places are a source of great expense to the producers, owing to damage suits by those whose crops or trees are injured thereby. This damage is usually denied, but the fact remains that the vicinity of a sulfide smelter is desolated.

Some years ago a careful study of the question led the senior author to believe that, in practically all cases, it is feasible to recover such fumes, that marketable products can be profitably produced in any locality where large smelters operate, that the value thus produced will in many instances exceed that of the metal produced, and that no other phase of the sulfuric acid industry is so important. Zinc smelters located in the Eastern and Central States have already profited largely by the use of this former waste. Two copper companies in the South have done something in the same direction; in 1935, they had capacity for producing 1500 tons (60° Bé.) a day. In 1929, zinc blende served as raw material for nearly 8% of the total U. S. production of acid, and copper ores more than 7%. In 1938, these ores produced 13% of the total acid.

The principal technical difficulties to be overcome in the utilization of conventional smelter gases are their low and variable strength of SO_2, the dust and metallic oxides (sometimes including precious metals) and the considerable content of carbon dioxide and sometimes carbon monoxide. Also many smelters are located so far from the centers of consumption of sulfuric acid that transportation of the acid is expensive. New smelters designed with an eye to abating the SO_2 nuisance by the utilization of the gases can produce gases of much higher and more constant SO_2 content, thus reducing the volume of gas to be handled and consequently the initial cost and operating cost of the acid plant. Rotary kilns and flash roasters for this purpose will be described under the heading "Burning of Pyrites and Sulfide Ores."

Gypsum and Anhydrite—Gypsum, though widely distributed and abundant, is not yet in use in this country as a primary raw material for sulfuric acid. In Germany, gypsum is heated with clay and coal, sand and slag being added; the resulting SO_2 gases are purified and used for acid-making.[23]

The I. G. Process based on the use of $CaSO_4$ has a yearly capacity of 65,000 tons SO_3 and 75,000 tons of cement. Clay is pre-dried to remove moisture and is then mixed and ground with anhydrite ($CaSO_4$) and coke into a raw meal whose composition is such as to permit complete reduction of the sulfate radical to SO_2, as well as to contain the correct mixture for a good quality cement. The charge is then roasted in a rotary kiln. The gas driven off is freed from foreign particles in large dust chambers and is cooled and washed in scrubbing towers. Air is then added to provide the necessary oxygen to form SO_3. From this point on, the usual SO_3 contact process with vanadium catalyst is used. Before 1940, three-quarters of Germany's annual 2,800,000

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[22] Chem. and Met. Eng., *45*, 24 (1938).
[23] Chem. and Met. Eng., *47*, 333 (1940).

metric tons of sulfuric acid came from pyrites; the remainder came from zinc and copper smelters, plus a small amount from sulfur in coal. Since the importation of pyrites then became uncertain, I. G. Farbenindustrie undertook large-scale production, using the Müller-Kühne process.

France is experimenting with similar plants. Russia[24] and India[25] have also undertaken the production of SO_2 from gypsum. If the anhydrite ($CaSO_4$) cement process proves to be commercially successful in this country, this may become an important source of SO_2.

Waste Products Used for Acid Manufacture—"Spent Oxide" is utilized largely in England. This is a mixture of ferric oxide, ferrous sulfide and sulfur, resulting from the use of ferric oxide to absorb hydrogen sulfide out of illuminating gas.[26]

Alkali waste from the Leblanc process,[27] containing calcium sulfide, has been utilized in England by the Chance-Claus process which produces H_2S; this is then burned to SO_2.[28]

Hydrogen sulfide from ammonium-sulfate plants has also been used in England.[29] The sodium phenolate purification process used in oil refineries also produces H_2S suitable for acid-making.[30, 31]

"Acid sludge," formed in large quantities at oil refineries, contains strong sulfuric acid and various hydrocarbons, naphthenes, phenols, etc.; the disposal of this has always been a serious problem. At large refineries it is feasible to recover the acid by separating and concentrating, as described later in this chapter. Alternatively, and especially for small tonnages, there are new methods developed by the Chemical Construction Co. of New York, which involve charring the sludge to coke (available for fuel) and SO_2, then making sulfuric acid from the gases.[32]

Ferrous sulfate liquors from steel and iron pickling and from titanium pigment manufacture are also produced in large quantity. The latter contain about 16% H_2SO_4 and 23% $FeSO_4$. For these, the Chemical Construction Co. has installed plants to roast the dried sulfate mixed with pulverized coal and manufacture acid from the gases produced. The Mantius Engineering Co. has installed large equipment to recover the $FeSO_4$ and H_2SO_4 by partially evaporating, crystallizing out the $FeSO_4$, then evaporating to 60° or 66° Bé.[33]

SULFUR BURNING

In burning sulfur, four points chiefly have to be considered: viz., freedom of the gases from volatilized sulfur which has not been oxidized; sufficient richness of the gases for profitable operation of the acid-making plant; con-

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[24] Chem. Abs., *32*, 6405 (1938).

[25] Chem. Abs., *32*, 313 (1938).

[26] See Chapter 15.

[27] See Chapter 10.

[28] Fairlie, loc. cit., p. 86; Kreps, loc. cit., p. 80.

[29] Fairlie, loc. cit., p. 86.

[30] Kreps, loc. cit., p. 266.

[31] Chem. and Met. Eng., *44*, 24, 79 (1937).

[32] "The Science of Petroleum," Oxford University Press, 1938, p. 2769.

[33] U. S. Patent 2,078,088.

stancy of gas richness; and as complete removal as possible of sulfur from the slight residue of mineral matter.

The desirable richness depends on several conditions, as will be discussed later. Chamber plants prefer to run at about 10% SO_2; contact plants run at 7 to 8% if extremely high efficiency is desired, or up to 10% if maximum output is needed. If a waste-heat boiler is used, the gas can come to it at 12% or 13% and be diluted afterward; thus the boiler gets the benefit of the higher temperature resulting from the richer combustion.

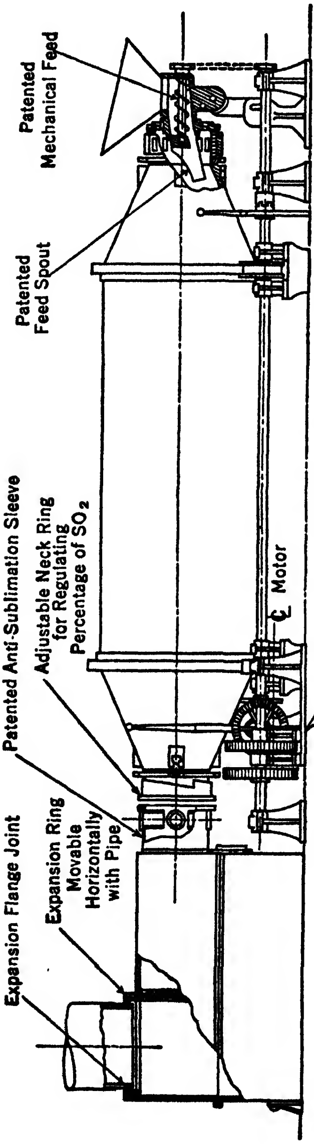

FIG. 4. Rotary Sulfur Burner.
Manufactured by Glens Falls Machine Works, Glens Falls, N. Y.

Rotary Sulfur Burner—The Tromblee & Paull, or Glens Falls, burner shown in Figure 4, consists of a horizontal cylindrical iron shell with conical ends, revolving on its axis once in two minutes. At one end is the hopper with its worm feed and sliding dampers. The other end connects with a rectangular cast-iron box provided with sliding damper and vertical cast-iron uptake pipe. The sulfur fed into the hopper needs no preparation other than breaking up large lumps with a shovel. When forced along by the worm, the sulfur melts just before it drops into the body of the burner, and a sufficient amount of melted sulfur is always present to form a complete liquid coating on the inside of the shell as it revolves. The combustion box and vertical uptake complete the combustion of any sulfur which is volatilized from the cylinder.

The special advantages of this burner are ease in controlling composition of gas, low cost of upkeep, and freedom from losses. Once in about two months it is necessary to clean out the dross which collects in the cylinder. To do this, or to prepare for a shut-down for repairs in any other part of the plant, the sulfur charge is allowed to burn out completely. Any residue in the cylinder is then easily removed by a hoe. Starting the burner after cleaning, or even when it is cold, is a simple operation, and no losses occur.

This type of burner has been widely adopted by American chamber plants and is one of the most satisfactory for use in induced draft systems, i.e., where the gas is sucked through the burner by a fan or blower located beyond it.

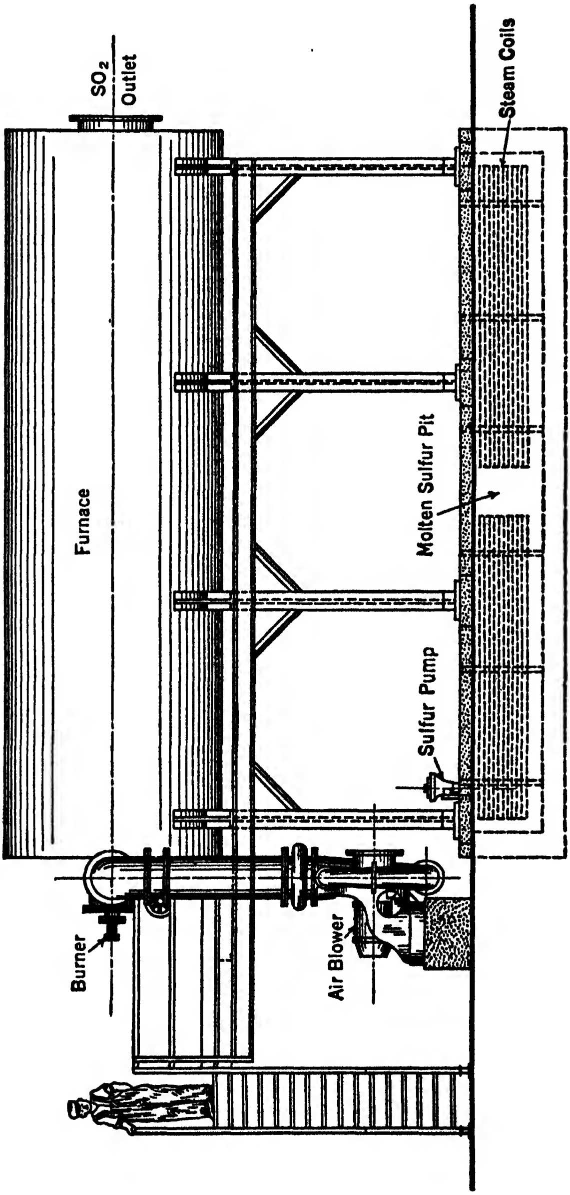

Fig. 5. Spray Sulfur Furnace.
(Patented) Manufactured by Chemical Construction Corp., Charlotte, N. C. Key: A, Steam Coils; B, Molten Sulfur Pit; C, Sulfur Pump; D, Burner; E, Air Blower; F, Furnace.

Pressure Burner, Spray Type—The forced-draft system of combustion, i.e., forcing the air into the burner and thence through the rest of the acid-making plant by means of a blower located before the burner, has definite advantages, especially for contact-process plants. It facilitates the use of predried air, since no inward leakage can occur. It eliminates the need of making the fan of materials resistant to sulfur dioxide. Also, since a centrifugal fan or blower develops a pressure proportional to the density of the gas handled, a blower handling cold air develops higher pressure at a given speed than when handling hot gas.

In 1927, Hechenbleikner introduced a forced-draft sulfur furnace (Figures 5 and 6) which has achieved great success. Molten sulfur is sprayed in through a burner which in many respects resembles the common spray-gun type oil burner. The sulfur is melted by steam coils in a large pit where impurities are removed by settling and by skimming. The molten sulfur is pumped by a small variable-speed centrifugal pump through a steam-jacketed pipe to the spray nozzle. The air for combustion is forced into the furnace at a pressure of 1.5 to 2 lbs. per sq. in. by a high-speed centrifugal blower direct-driven by a steam turbine or a motor. The quantity of sulfur consumed and the strength of the sulfur-dioxide gas can be controlled closely by regulation of the sulfur pump and the blower. Since the sulfur burns in a spray as it leaves the nozzle and there is no bed of molten sulfur in the furnace, this type of furnace has the further advantage that, in an emergency, the gas flow can be stopped instantaneously, whereas furnaces containing a body of sulfur can only be shut down after some delay.

FIG. 6. Spray Sulfur Furnace, Blower, Melting Pit and Sulfur Pumps. (Courtesy Chemical Construction Co.)

Waste Heat Boiler—Since, in a contact plant, the sulfur-dioxide gas must be cooled somewhat before it can be sent to the converter, the exit gases from the furnaces are usually passed through a waste-heat boiler where they generate the steam used for melting the sulfur and driving the sulfur pump. With careful engineering design, in a plant of 80 tons daily acid capacity or larger, enough steam can be obtained to drive the blower also, resulting in a large saving in power cost. The most desirable arrangement is to produce burner-gas of about 12% SO_2, pass this through the boiler, then dilute it with air to 7% or 8% for the converters. This gives in practice a furnace temperature of about 1015° C. (1860° F.) instead of 640° to 720° C. (about 1180° to 1330° F.) and the increased temperature difference between gas and steam enables the use of a much smaller boiler and the production of slightly more steam.

Some of the early waste-heat boilers caused trouble because leakage of steam from the joints of the boiler entered the gas stream. Moisture in the gas is highly objectionable, as it lowers the dewpoint of the gas, so that liquid sulfuric acid may be deposited in cooler parts of the plant and cause corrosion. Such acid will also ruin a vanadium-oxide catalyst by forming sulfate.

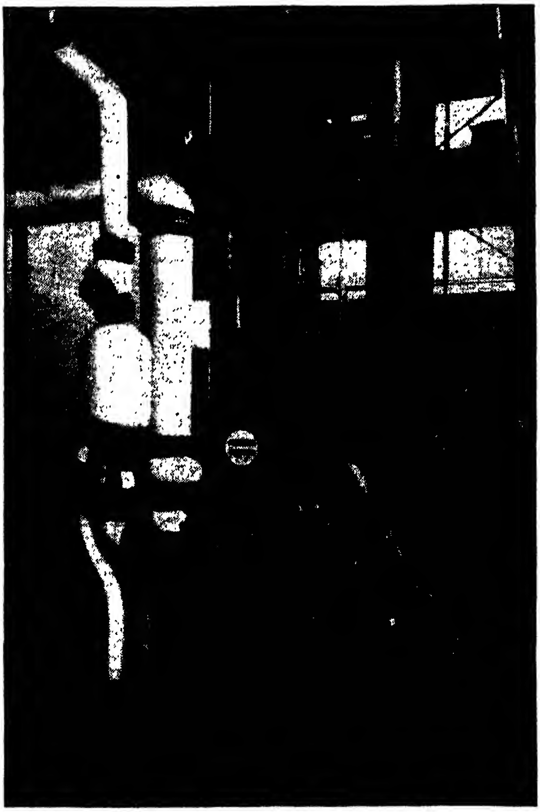

FIG. 7. Centrifugal Blower, Turbine-driven.

In 1930, boilers of a new type, developed by the junior author of this chapter in collaboration with the Foster-Wheeler Co., were installed for the American Cyanamid Co. In these boilers (Fig. 8), all joints and tube-ends were outside of the gas stream, so any steam leaks would blow harmlessly into the atmosphere, and incidentally be accessible for repair. Automatic valves prevented drawing steam from the boiler unless the pressure was over 175 lbs. per sq. in.; thus the metal surfaces in contact with the gas were kept hotter than the dewpoint of even a very imperfectly dried gas and corrosion was prevented. The steel tubes were further protected against corrosion by cast-iron rings shrunk on. These rings were provided with fins to increase the surface for heat transfer[34] from the gas, since the gas temperature is low and the heat-transfer coefficient from gas to a surface is very much less than that from a surface to boiling water. This design was based on Foster Wheeler's waste-heat boiler, in which the hot gas stream passes up through an approximately cubical chamber closely packed with finned horizontal water-and-steam tubes between which the gas flows. In this sulfur-gas boiler, the tubes were hairpin-shaped, i.e., in the form of a long "U." The two ends of each hairpin passed out through the gas-tight wall of the chamber and joined, entirely outside of the wall, into headers leading to the steam-and-water drum. The gas chamber was designed for a pressure of 4 lbs. per sq. in.

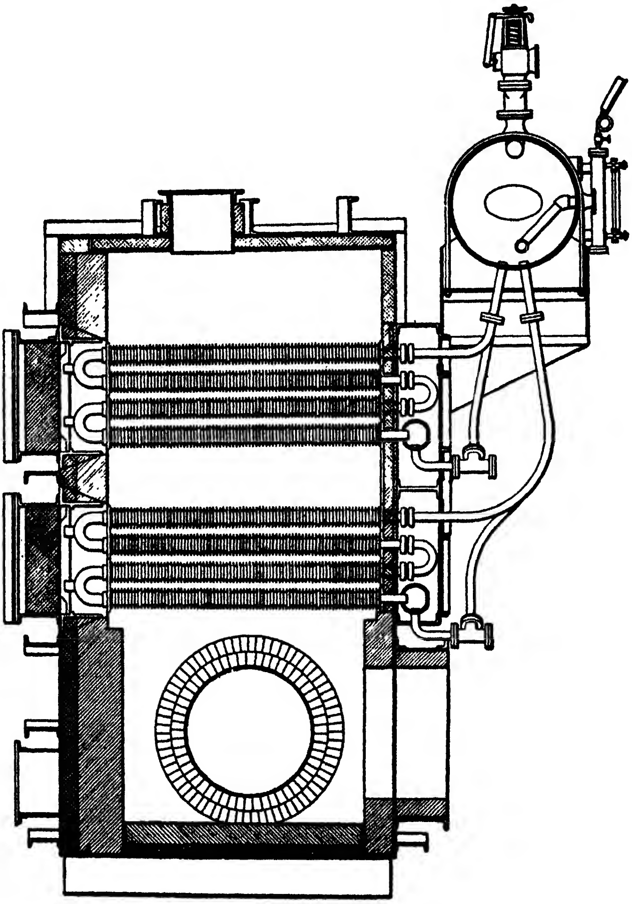

FIG. 8. Leakproof Waste Heat Boiler with Tubes Protected by Cast Iron Finned Sleeves and Return-Bends. Gas inlets at bottom, outlet at top. (Courtesy Foster-Wheeler Corp.)

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[34] For a discussion of the principles of this type of heat transfer see Chapter 2

Burning of Pyrites and Other Sulfide Ores—The use of pyrites has become of comparatively small importance in this country, but the urge among copper and zinc smelters to make sulfuric acid instead of discarding their sulfurous gases has focused attention on means of roasting these ores so as to produce gases better adapted to acid-making. The latter problem is similar to pyrites-burning.

Burners or furnaces for pyrite and other sulfide ores are of several classes. Lump pyrite was formerly burned on grates like coal; in recent practice the pyrite is ground to ¼″ or ½″ and burned in mechanically-raked hearth furnaces; recently, rotary kilns have been installed to handle sulfide ores from 10-mesh down to include most flotation concentrates.[35] For very fine ores "flash roasters" are used, in which the pulverized ore is blown from a nozzle into a combustion chamber.[36]

Mechanical Fines-Burners. The mechanical furnace with vertical shaft was developed by McDougall in England and by Perret in France in the 1870's. Modifications were made and patented from time to time by these inventors, by Mackenzie, Frasch, Herreshoff, Spence-Skinner, Lurgi (Germany), and others. Two furnaces widely used are the Herreshoff (Nichols Engineering & Research Corp.) and the Wedge (Bethlehem Foundry & Machine Co.). These are sufficiently similar that the following description will serve for both.[37] The Wedge can also be obtained in a water-cooled design.

This furnace (Figure 9) has a vertical, cylindrical steel shell, lined with firebrick; inside this shell eight to sixteen brick hearths are placed one above the other. The topmost hearth, which merely dries and preheats the ore, is open to the atmosphere. The others are enclosed, the gas passing up from one to the other and out above the next-to-topmost. A hollow air-cooled shaft, rotating very slowly on the vertical axis of the shell, carries two or four radial arms over each hearth. To the under side of the arms are attached rabble teeth or plows almost touching the hearth. These are set at an angle so that, as each tooth plows through the shallow layer of pyrite ore on the hearth, it moves the ore radially by the width of a furrow. The ore is continuously fed in near the center of the top hearth, and by the repeated plowing is gradually moved out to the periphery, where it falls through openings to the next hearth below. On this next hearth the teeth are set to move the ore inward toward the center, where this hearth has its discharge opening. Thus, being plowed alternately outward and inward on successive hearths, the roasted ore finally arrives at the bottom discharge opening. In usual practice, the roasting is not quite complete, the cinder containing 2 to 3% sulfur.

Ores containing 30% of sulfur or more will burn in these furnaces without any other fuel. If the sulfur content is over 40%, e.g., pyrites, which usually contains 45 to 50%, the normal heat of combustion would introduce danger of overheating the arms and teeth and clinkering the ore. Therefore the shaft and most of the arms are made double-walled, and air is circulated through them for cooling. After passing through these arms, the air is returned hot

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[35] Fairlie, loc. cit., p. 107.

[36] Fairlie, loc. cit., pp. 115-121.

[37] For a discussion of the function of roasting in nonferrous metallurgy see Chapter 24.

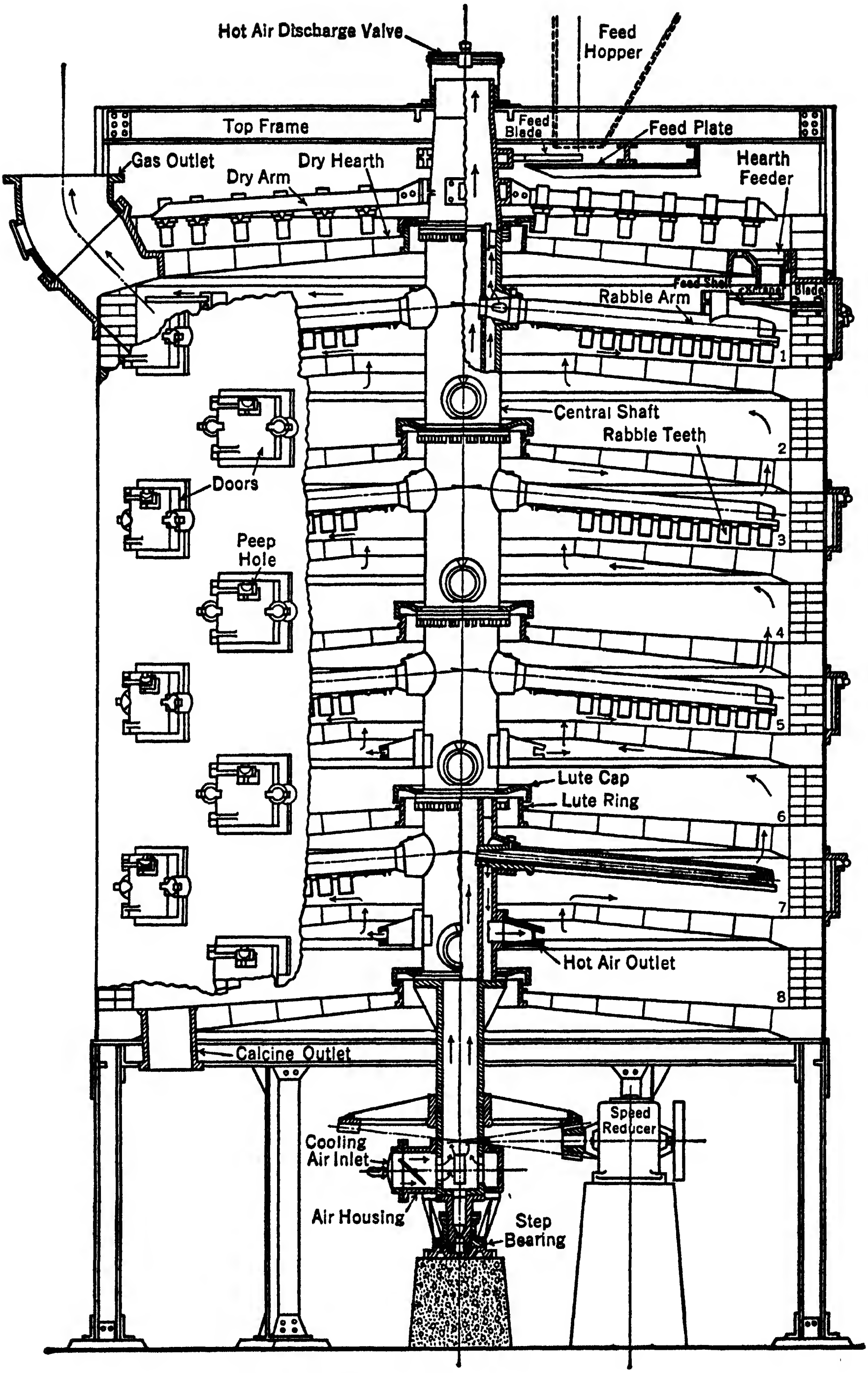

FIG. 9. Herreshoff Air-cooled Furnace.

to the shell of the shaft and may then be discarded through the top of the central shaft or diverted and discharged through hot-air arms on the lowermost hearths where the ore is sulfur-poor. With the four-arm-outlet design any combination of rabble arms, cooling arms, or hot-air arms can be obtained. This affords a very flexible arrangement. Such arm outlets as are not used may be blanked off by closing plugs which are furnished for this purpose. The arms and teeth are removable and replaceable through small doors in the wall; a man enters the hollow shaft to remove the nuts holding the arms. In recently built furnaces, the use of special heat-resisting irons and steels permits operation at higher temperatures than before.

Rotary Kilns for Fines. The horizontal rotary kiln[38] is used for pyrites and other sulfide ores. It is most satisfactory on ores of 10- to 80-mesh, but is also said to handle 200-mesh flotation pyrite by sintering[39] it as described below. It is like a cement kiln, viz., a steel cylinder, sometimes as large as 11 feet in diameter by 110 feet long, lined with fire-brick. The cylinder is slightly inclined downward from the feed end; it rests on rollers and is power-driven at a speed of one or two revolutions per minute. The ore is fed in at the higher end and gradually works its way down to the other. Scoops attached to the walls lift the ore by the rotation of the cylinder and spill it in a shower through the gas. With pyrite, the aim is to form nodulized Fe_3O_4 cinders of ¼″ or so, minimizing the formation of dust. This is accomplished by mixing some previous cinder with the ore fed in, and by keeping the temperature close to the sintering point. At too low a temperature, the ore remains as fines or dust; at too high a temperature, large clinkers are formed. In any case a certain amount of dust is formed, necessitating a wet purification of the gas. The sulfur content of the cinder is only about 0.5%.

In Germany, many kilns of this type, made by the Lurgi Gesellschaft, are in operation on various sulfide ores. In the United States, the Chemical Construction Co. has a number of installations, including some for handling oil-refinery sludge and some for ferrous sulfate from the waste liquors of pickling plants.

Flash Roasters. For very fine material such as the 200-mesh pyrite separated from copper ores by the flotation[40] process, flash roasters are coming into use. In the Nichols-Freeman system (Nichols Engineering and Research Corp., N. Y.) the fine wet pyrite is dried in a ball mill by preheated air and blown into the top of a vertical, cylindrical combustion chamber, into the bottom of which air is fed for secondary combustion. Here the pyrite burns, forming principally Fe_3O_4, which, due to the sudden high temperature (1100° to 1150° C.), fuses into bubbles of pinhead size and falls to the bottom.[41] Some red dust, probably Fe_2O_3, is formed; this passes out with the gas. The gas is cooled by a waste-heat boiler, then undergoes a complete purification. The cinder contains only about 0.5% sulfur.

For zinc-sulfide flotation concentrates, a large installation of flash roasters

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[38] Fairlie, loc. cit., pp. 107 and 550.

[39] For a description of another widely used type of sintering machine see Chapter 24.

[40] See Chapter 24.

[41] Trans. Amer. Inst. Chem. Eng., *33*, 187 (1937).

was made in 1928-31 at Trail, British Columbia, by the Consolidated Mining and Smelting Co. of Canada.[42] Since zinc roasting produces much more dust than does pyrites, the waste-heat boiler was omitted, and cyclone separators and Cottrell electrostatic precipitators were used on the hot gases. Due to the high rate of combustion, the zinc concentrates are thoroughly roasted without the use of any other fuel. This is difficult or impossible to achieve in any other type of furnace now in use, the original sulfur content of the ore being so low.

Dust Removal and Purification of Gases—In a chamber-process plant, dust and sublimed sulfur carried by the gases into the Glover tower are objectionable, but not prohibitively so. They are absorbed by the acid; part settles out as sludge in tanks, pipes, pumps, etc., and part remains as impurity in the acid sold.

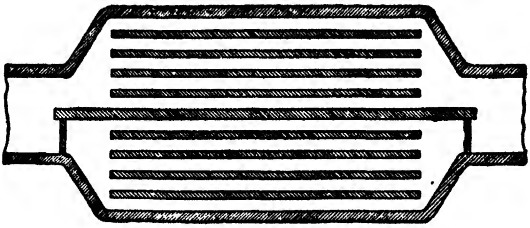

FIG. 10. Howard's Dust Separator.

In a contact plant, however, dust reaching the converter will coat the catalyst and seriously affect its performance. It is therefore customary to carry out such a good removal of dust that a Tyndall test shows none, i.e., a beam of light as strong as sunlight passed through the gas is invisible. Furthermore, the older varieties of platinum catalyst require that various volatile substances that would "poison" them, especially arsenic, chlorine and fluorine, must be condensed and scrubbed out. Finally, the gas must be filtered to remove sulfuric-acid mist, and dried by strong sulfuric acid. These processes will be described later, under the heading of Contact Process.

Settling Chambers. Older plants used large settling chambers to reduce the velocity of the gas and so to permit at least the coarser dust to settle out. A more effective device, but troublesome to clean, consists of a series of horizontal parallel shelves an inch or so apart, across which the gases pass in a slow stream, from a general inlet chamber to a general outlet chamber. The principle is that of shortening the distance through which the dust has to fall in order to be deposited.

Cyclone Dust Collector. Cyclone dust collectors are used in many modern plants to remove the coarse dust. They occupy much less space and are cheaper than settling chambers. They consist of a vertical cylindrical chamber with a deep conical bottom. The gas enters tangentially at the top at high velocity and is drawn off at the center by a pipe extending part way down into the chamber. The dust is thrown against the walls by centrifugal force and falls into the conical bottom whence it can be removed without

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[42] Ind. and Eng. Chem., *24*, 717 (1932).

stopping the flow of gas. By the use of a number of small cyclones in parallel instead of one large cyclone, somewhat finer dust can be separated, because the centrifugal force is greater and the dust has less distance to travel to reach the wall.

Cottrell Electrostatic Dust Precipitator. The Cottrell system of electrostatic precipitation[43] is capable of removing the finest dusts from gases, as well as droplets of liquid constituting a mist, and in commercial practice removal of 95 to 97% of the total amount of dust is attained. Impurities existing as gases (e.g., arsenious oxide at high temperature) are of course not removed. The apparatus is quite expensive, and is customarily used as a dust remover only where the value of the dust is appreciable, e.g., zinc oxide in plants making acid from zinc-sulfide ores. It is however almost universally used when the removal of sulfuric acid mist from cooled gases is required at later stages of the process of acid-making.

In the usual Cottrell, the gas is passed in parallel through a great number of small vertical metal pipes each having a wire hung in its center. The pipes are electrically grounded, and a unidirectional voltage of 50,000 to 80,000 volts is applied to the wires. The particles of dust are electrostatically attracted to the pipes. At regular intervals the unit is cleaned, one section at a time, by shutting off the gas stream and the voltage, and mechanically rapping the pipes to dislodge the particles. Another form of the Cottrell precipitator uses parallel plates instead of pipes. The power consumption is small, about 5 to 8 KWH per million cubic feet of gas.[44]

Gases as hot as 500° C. can be handled in the standard steel apparatus. By using special metals (chrome-steels, etc.), 600° C. gas can be handled. In handling dusty burner-gases the temperature should be kept above the dew-point of the gas; otherwise sulfuric acid droplets may be deposited on the electrodes as well as dust, making a coating not removable by rapping. With well-dried gas (3 to 5 milligrams of water vapor per cubic foot) the dew-point of the gas is 125° to 135° C., but with 100 milligrams it is about 200° C.

THE CONTACT PROCESS OF MANUFACTURE

The "contact" process is increasingly being used for sulfuric acid manufacture. The name is derived from the fact that the reaction, or group of successive reactions, by which the SO_2 in the burner gas is oxidized by the O_2 therein, takes place *in contact with* the surface of a solid catalyst. The reaction is strongly exothermic, and is usually carried out at temperatures between 400° and 550° C., as will be discussed later.

Early History—We are apt to think of the contact process as a development of the last thirty years, overlooking the enormous amount of effort that for nearly a century was spent in the right direction, but just missed some little step which was important. Peregrine Phillips, in 1831, patented the oxidation of sulfur dioxide by passing it with excess of air through a tube containing hot finely-divided platinum.

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[43] See Chapter 2 and Chapter 15.

[44] Fairlie, loc. cit., p. 139.

Until about 1870, however, there was no great commercial demand for very strong sulfuric acid such as is made by the contact process, and the little that was required was made by distilling sulfates. Then the demand came with the invention of alizarin.[45] In 1875, Clemens Winkler described his own attempt to synthesize SO_3, recommending platinized asbestos for the purpose. Unfortunately, despite the "Law of Mass Action," even then well known, he stated that stoichiometric proportions of gases should be used. We know today that, as taught by that law, and as will be quantitatively discussed later in this chapter, it is the excess of oxygen present with these gases which gives us as complete a conversion as is now commercially obtained. The increasing demand for concentrated acid led to a great deal of research and development on the contact process, much of it being shrouded in the utmost secrecy. Progress was very slow, much of the early difficulty being due to the acceptance of Winkler's erroneous theory. Finally, the principal platinum-catalyst systems were patented about 1900. The history of the developments of the process has been summarized in various places.[46, 47, 48, 49]

CATALYSTS

Poisoning of Catalysts—Early investigators found that arsenic trioxide and arsine "poisoned" the platinum catalysts, largely reducing their powers of conversion. A catalyst so poisoned had to be rejuvenated by chemical treatment to remove the arsenic, a long and expensive process. The volatile compounds of selenium, antimony, lead, and some other metalloids, have a similar poisonous effect though less severe. Chlorine, hydrochloric acid, and hydrofluoric acid are temporary poisons; i.e., the lessening of activity which they cause gradually disappears on passing gas free from the poison. Silicon tetrachloride deposits silica which, like dust or any other suspended matter, covers the contact mass from ready access to the gases. All early contact plants, therefore, required elaborate purification equipment to remove the poisons from the burner gas.

Poisoning has been stated by Langmuir to be due to the formation of a "monatomic" film of the poisoning substance over the active surface of the catalyst. Thus a very small amount suffices to reduce the activity of the catalyst very seriously.

It is claimed by Merriam[50] that if the burner gas reaches the converter without ever having been cooled to the condensing point of arsenic vapor or of sulfuric acid, these substances lose their power to poison a platinum catalyst. If this system be found practical, it will permit the elimination, at least in brimstone plants, of the expensive cooling, purifying and reheating operations customarily used to protect a platinum catalyst.[51]

[45] See Chapter 28.

[46] Berichte, *34*, 4069-4115 (1901).

[47] Wells and Fogg, loc. cit., pp. 150-151; 169-174; 181-183.

[48] Miles, F. D., "Manufacture of Sulphuric Acid" (Contact Process), D. Van Nostrand Co., 1925, pp. 289-410.

[49] J. Soc. Chem. Ind., *41*, 106 T (1922).

[50] Fairlie, loc. cit., p. 517.

[51] Thompson, Trans. Amer. Inst. Chem. Eng., *27*, 286 (1931).

Iron-oxide catalyst is not injured by arsenic, but it is such a weak catalyst that in practice it can only be used for partial conversions.

The first successful catalysts practically immune to poisoning by arsenic and by chlorine were those using vanadium pentoxide instead of platinum. Platinized silica gel, a catalyst recently developed, also has been found immune to arsenic.

Vanadium Catalysts—As early as 1895 the use of vanadium catalysts was suggested for oxidation of SO_2. The earliest patent covering this type of catalyst was granted to deHaen in Germany in 1900. As early as 1904, Küster recognized the freedom from poisoning of vanadium catalysts as compared with platinum. Although there was a considerable amount of investigation of vanadium catalysts carried on in Europe before the War of 1914-18, there seems to have been no particular interest in them displayed in this country, nor any commercial importance attained by them until after the War. Since 1920, America has taken the lead in this direction.

At first, difficulties were experienced in the United States in the attempts to use vanadium catalysts and get commercial yields. These difficulties have been overcome within the last fifteen years by the development of new types of converters permitting closer temperature control, and by improved catalysts. These developments have resulted in a great increase in the relative number of contact-acid plants in the United States since 1927 and have revolutionized the American sulfuric-acid industry, since they have so simplified the contact-acid process as to permit the manufacture of 66° Bé. (93%) acid more cheaply by dilution of contact-plant acid than by concentration of chamber acid.

Composition of Vanadium Catalysts. The active agent in vanadium catalysts is vanadium pentoxide or salts thereof such as sodium vanadate. The chemical action is presumably reduction to one of the lower oxides of vanadium and re-oxidation to pentoxide. Commercial catalysts contain a "promoter," usually a compound of potassium, which very greatly increases the catalytic activity. The correct proportion between the promoter metal and the principal metal (vanadium) is very critical.[52] Other promoter metals have been proposed, notably thallium,[53] calcium,[53] and barium,[54] also other vanadates such as silver,[55] copper,[55, 56] and tin.[57]

The completed catalyst, or "contact mass," is in the form of granules or pellets the size of a pea. These granules (the "support" or "carrier") must be porous to permit access of gas to the interior of the granule. However, they must be strong enough so that neither mechanical handling nor the strains caused by heating and cooling of mass or converter will fracture them or break off small particles. Such formation of dust or fines in a commercial converter

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[52] Griffith, R. H., "Mechanism of Contact Catalysis," Oxford Univ. Press, 1936, Chap. III.

[53] Adadurov, I. A., and Formicheva, J. Appl. Chem., (U. S. S. R.) *10,* 988-998 (in German 998).

[54] Chem. Abs., *28,* 5603, 4182.

[55] Maxted, E. B., "Catalysis and Its Industrial Applications," London, 1933, p. 491.

[56] Neumann, B., Kroger, C., and Ivanowski, R., Z. Electrochem., *41,* 821 (1935).

[57] Maxted, E. B., and Hassid, N. J., J. Soc. Chem. Ind., Oct. 23, 1931, p. 400 T.

will choke the interstices between the granules and interfere with the uniformity of distribution of the flow of gas, thus causing local overheating.

The Selden Catalyst. The Selden vanadium catalyst and Jaeger's "automatic temperature control" converter are now marketed by the Chemical Construction Co., New York, as part of their standard contact plants. About seventy-five plants have been built in the United States and abroad. The catalyst is made as follows.[58] Kieselguhr is sprinkled first with potassium-silicate solution, then with potassium-aluminate solution, forming a jelly-like zeolite of potassium-aluminum silicate containing particles of kieselguhr. This is forced through a screen to form it into lumps, over which is then poured a thick solution or suspension of ammonium vanadate. This mixture is passed between rollers and through a screen. It is then formed under heavy pressure in a pill-making machine into pellets about 3/16″ diameter by 3/16″ long. The pellets are then heated in a stream of dilute SO_2 and air, care being taken to keep the temperature from going above 500° C.

The Monsanto Catalyst. The Monsanto mass is understood to be made from ammonium vanadate, potassium hydroxide, and waterglass, with a carrier such as kieselguhr. It is marketed as pellets of the same shape as the Selden mass.

K. F. I. Catalyst. The General Chemical Co.'s "K. F. I. Catalyst"[59] is said to be made by absorbing alkaline sodium-vanadate solution in a dry mixture of kieselguhr, potassium sulfate and gum tragacanth, neutralizing with sulfuric acid, drying, pelleting and calcining at 600° C.[60]

The Calco Catalyst. The "Calco" catalyst[61] consists of large (1/4″ to 3/8″) chips of natural diatomaceous earth, fired at 1000° C. to strengthen them, and impregnated with compounds of vanadium and of alkali metals. These chips are said to be less friable than catalysts made by pelleting powdered material. The Calco catalyst is claimed to give conversions as good as other vanadium catalysts; tests made in the senior author's laboratory have confirmed this.

Chromium-Tin Catalyst—Recently there has been considerable activity in Russia to develop catalysts without vanadium. Cr-Sn-Ba is said to be as good as vanadium; for Cr-Sn-K and Cr-Sn-Fe, good conversions are also claimed.[62, 63, 64, 65] They are said to be as resistant to poisoning as the vanadium catalysts.

Platinum Catalysts—The earliest work on the oxidation of SO_2 to SO_3 was done with platinum catalysts, and they have quite extensive commercial use. However, on account of the great cost of the platinum used in a contact mass, it is necessary that it be recoverable from a discarded or poisoned mass. Only three "carriers" have been found that permit this to be successfully done, viz., asbestos fibre, magnesium sulfate, and silica gel.

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[58] Fairlie, loc. cit., pp. 414, 415.

[59] U. S. Patent 1,887,978.

[60] Fairlie, loc. cit., p. 415.

[61] U. S. Patent 1,862,825.

[62] Adadurov, I. A., J. Chem. Ind. (Moscow), *11*, 53-55 (1934).

[63] Adadurov, I. A., J. Appl. Chem. (U. S. S. R.), *7*, 875-880 (1934); Chem. Abs. *28*, 4182.

[64] Adadurov, I. A., and Gernet, D. V., ibid., *8*, 606-610, 612-626 (1935) (in German 611, 626-627).

[65] Gernet, D. V., and Khitun, A., ibid., *8*, 598-604 (1935) (in German 605).

Platinized Magnesium Sulfate (Grillo-Schroeder Mass). Magnesium sulfate is calcined, ground fine, mixed to a thick cream with water, and again calcined in a red-hot pan with constant rabbling. This forms porous lumps, hard and non-friable. Lumps of half-inch size are selected by screening, sprayed with platinic-chloride solution, and placed in the converter. On heating, metallic platinum is formed.

Another method is to mix the platinic chloride with the magnesium sulfate before calcining. This distributes the platinum better throughout the mass, but some platinum is lost in the screening operations. Both methods are described in detail by Miles[66] and by Wells and Fogg.[67]

In early plants, 26 to 28 troy ounces of platinum were used per daily ton of H_2SO_4; by 1920, due to improvements in design, 13 ounces were found sufficient; nowadays, 5 to 6 ounces suffice. The concentration of platinum in the mass is usually 0.1 to 0.3%; in some plants, to avoid overheating in the first stages of the conversion, where the reaction is more intense, a less concentrated mass is used there.

Temporary poisoning by free chlorine does not ruin the mass; its activity can be restored by passing chlorine-free gas through it at high temperature for some hours. Slight arsenic poisoning can be removed by filling the converter while hot with chlorine gas and letting it stand a day, then passing hot gas for another day. For more severe arsenic poisoning, the mass is removed, sprayed with aqua regia, and replaced. Both of these methods depend on the volatilization of the arsenic as chloride. However, if the mass has been contaminated by so great a quantity of arsenic that neither these treatments nor grinding and recalcining will permanently restore its activity, it must be discarded. In this case, of course, the platinum is recovered by dissolving in acids, reducing to metal, and redissolving as platinic chloride.[68]

Platinized Asbestos. The preparation of platinized asbestos is simple in theory, but in practice is something of an art. Long-fibred asbestos, preferably Italian, is washed with hydrochloric and nitric acids, then soaked with a 10% solution of platinic chloride containing a reducing agent, such as glucose or sodium formate, and heated.[69] The asbestos is sometimes woven in the form of rope mats, sometimes merely fluffed into a loose mass. In the converter, the gas passes downward through a number of shallow layers of the asbestos, each layer supported on a perforated tray. Thus, the gas is well distributed.

The amount of platinum required per daily ton of acid is about the same as with magnesium sulfate, having paralleled it as the art has developed. The asbestos usually carries 6 to 10% of its weight of platinum.

Working on properly purified gases, a well-made asbestos mass should remain in place 10 to 15 years.

Chlorine poisoning is treated as for Grillo mass. Permanent poisoning results if arsenic oxide reaches the mass; when this occurs, the mass (or at least the initial tray-loads) must be replaced by fresh mass. A slight poison-

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[66] Miles, loc. cit., p. 132 ff.
[67] Wells and Fogg, loc. cit., p. 174 ff.
[68] Miles, loc. cit., pp. 140-144.
[69] J. Soc. Chem. Ind., *41*, 106 T (1922).

ing by arsenic can sometimes be cured by washing the asbestos with hydrochloric acid.

Platinized Silica Gel. The "glassy" silica gel of W. A. Patrick[70] has great promise as a carrier for platinum. It is made[71] by mixing solutions of water-glass and of hydrochloric or sulfuric acid, both at the proper concentrations, whereupon a clear, firm gel is obtained. This is broken into pieces, washed, and dried at 300° to 400° C. or under vacuum at 75° to 120° C. The product resembles broken glass in appearance, but has an enormous number of ultra-microscopic pores. It is next treated with a reducing gas (e.g., SO_2 or H_2) which fills the pores, then is sprayed with a platinum solution, and heated to form metallic platinum. As usually prepared, it contains 1/8 of 1% by weight of platinum; 1½ to 3⅞ ounces of platinum per daily ton of H_2SO_4 are used.

Chlorine has the same poisoning effect as on other platinum catalysts, and fluorine or hydrofluoric acid destroys the gel. However, it is said to be totally immune to arsenic. This property, and the small amount of platinum required, should make its use increasingly popular.

Vanadium vs. Platinum—The question of the relative desirability of vanadium vs. platinum as catalyst has been a highly controversial subject, and is still a complicated one. Until 1927, platinized asbestos and platinized magnesium sulfate were the customary catalysts. Vanadium was introduced in 1927; with its freedom from arsenic poisoning it captured the market till the general economic depression of 1929. During this period, however, the price of platinum declined from $120.00 per troy ounce (January, 1926) to $36.00 (January, 1931), and now (July, 1941) it is still $36.00. Recently, platinized silica gel, claimed to be immune to arsenic, has come on the scene. Obviously, the question for any particular projected plant is "What catalyst will enable this plant to make the kind of acid required at the least cost, including interest and amortization?"

A catalyst susceptible to arsenic requires apparatus for thoroughly purifying the gas. This is expensive to build, costs something to operate, and with most systems wastes all of the heat in the burner gas. However, if the plant in question is required to make arsenic-free acid, the gas must be purified anyhow, or care taken to use a brimstone practically free from arsenic, such as that of Texas.

Platinum is expensive, but 85 to 90% of it is recoverable in salvage. Vanadium catalysts are made from relatively cheap materials but, inasmuch as they were privately developed and are patented, royalty charges are high. Vanadium masses have little or no salvage value. The total cost of platinum catalyst over a period of years can be much less or much greater than vanadium catalyst, depending on the market price of platinum and the royalty charged for the vanadium catalyst. For example, for a plant to make 100 tons of H_2SO_4 per day with platinized asbestos at 5½ oz. per ton, 550 ounces of metallic platinum would have cost $19,250 in August, 1939, and the asbestos and the preparation of the catalyst would cost about $9000, making a total of about $28,250 without allowance for the salvage value of 85 or

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[70] U. S. Patent 1,297,294.
[71] Fairlie, loc. cit., pp. 392-397.

90% of the platinum. In January, 1926, with platinum at $120 per oz. instead of $35, this catalyst would have cost $75,000.

It is often stated that vanadium catalysts cannot effectively handle gases stronger than 8% SO_2, whereas platinum handles 10%, the latter enabling greater acid production in the same size plant. Proponents of platinum sometimes state that the increased production is in direct ratio to the gas strength and that the only increased cost is that of the sulfur burned; obviously, these statements neglect the extra equipment and cost for burning the additional sulfur and handling the additional acid in process. It is also claimed that low gas-strength increases the resistance to gas flow in proportion to the square of the gas volume and thus greatly increases the power cost of gas handling. This is true in an existing plant, but if low gas strength is contemplated, the converters, heat exchangers, piping, etc., can be properly designed for it, in which case the increased volume of gas increases the power cost in direct ratio only.

The conversions obtained in a new plant should be the same with platinum as with vanadium, given suitable gas strengths, proper quantities of catalyst, competent design of apparatus, and careful operation. However, vanadium partisans claim that during the course of years plants using poisonable platinum catalysts usually find their conversion falling off.

Dust in the gas gradually injures both vanadium and platinum masses by covering their active surface. With vanadium, this can be partly cured merely by removing the mass, screening it, and replacing it.

Platinum, as will be set forth later, has a lower temperature coefficient of activity than vanadium, thus its effectiveness is not so easily disturbed by accidental variations in temperature. Also since platinum "ignites" (i.e., initiates the catalytic reaction) at a lower temperature than vanadium, less preheating of the gas is required.

GENERAL THEORY OF THE CONTACT REACTION

The equilibrium conversion (i.e., the maximum conversion possible to obtain in infinite time) is dependent on a number of factors, viz.:

1. The percentage by volume of O_2 in the entering gas.
2. The percentage by volume of SO_2 in the entering gas.
3. The pressure existing in the system.
4. The temperature at the reaction zone.

The closeness of approach to this equilibrium, being dependent on the velocity of reaction, is influenced by all of the above factors and also by:

5. The "load-rate," usually designated "space velocity," i.e., volumes of gas per hour per unit volume of catalyst including interstitial voids.
6. The linear velocity of the gas through the catalyst.

The actual "velocity of reaction" of course decreases asymptotically to zero as the reaction approaches equilibrium. At any given distance from equilibrium, it is inversely proportional to the "load rate" if linear velocity is kept constant, and according to some authorities[72] is directly proportional to a

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[72] Chang, H. Y., Abstract of Sci. and Tech. Pub., Mass. Inst. of Tech., No. 6, July, 1930, pp. 49-53.

fractional power of the linear velocity if load rate is kept constant. It also increases greatly with temperature up to an optimum temperature which is different with different catalysts.

Equilibrium of the Conversion—According to Guldberg and Waage's "law of mass action," the equilibrium of the reaction $2SO_2 + O_2 \rightleftarrows 2SO_3$ is given by the equation

$$K = \frac{[SO_3]^2}{[SO_2]^2 \cdot [O_2]} \qquad \text{(Eq. 1)}$$

in which $[SO_3]$, $[SO_2]$ and $[O_2]$ are the partial pressures of the respective gases, or, unless the reaction occurs at other than atmospheric pressure, the percentages by volume of these gases in the mixture. K is a constant at any one temperature, but decreases greatly as the temperature increases.

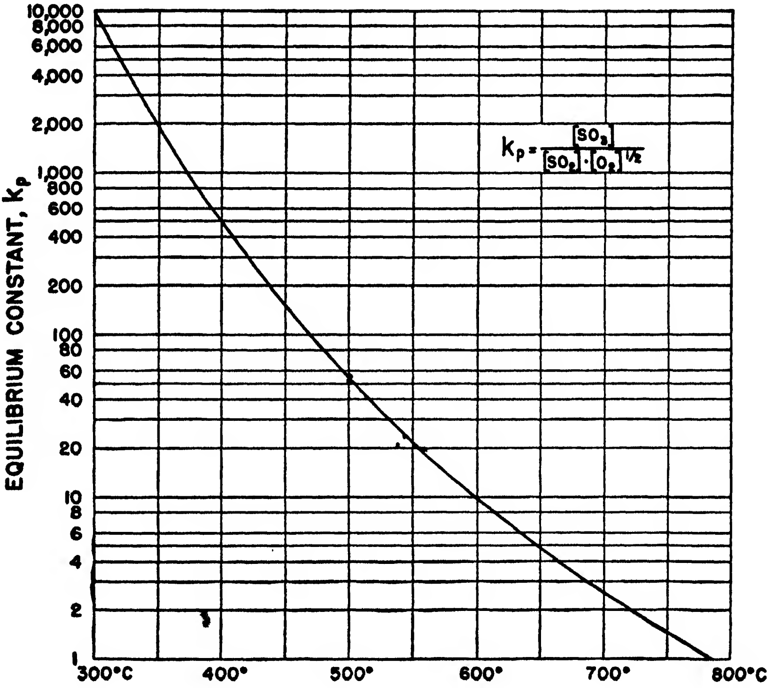

FIG. 11. Equilibrium Constant of the Contact Reaction.

This equation can also be based on one molecule of SO_2 and one-half molecule of O_2, in which case it is written

$$k = \frac{[SO_3]}{[SO_2] \cdot [O_2]^{1/2}} \qquad \text{(Eq. 2)}$$

The *k* thus defined has, of course, different numerical values from that in the previous equation. In using published values of the equilibrium constant, one must be careful to note what equation is used to define it. This equation may be transposed to

$$\frac{[SO_3]}{[SO_2]} = k[O_2]^{1/2} \qquad \text{(Eq. 3)}$$

from which it is apparent that the ratio of SO_3 to SO_2 and hence the percentage yield, or "conversion," at the termination of the reaction is greater the greater the percentage of residual oxygen. "Conversion" is the customary term for "amount of SO_2 oxidized, expressed as a percentage of the total SO_2 entering the process."

Several authorities have given different equations, based on experimental data, for predicting the value of k at a given temperature. On the basis of experimental work done in our own laboratory, we have chosen the one given by Miles,[73] viz.:

$$\log_{10}k = \frac{5186.5}{T} + 0.611 \log_{10}T - 6.7497 \qquad \text{(Eq. 4)}$$

in which T is the absolute temperature.

From this equation values of k were obtained which have been plotted against Centigrade temperature in Figure 11.

Calculation of the Equilibrium. The results of laboratory tests and commercial work are usually expressed in "% conversion," i.e.,

$$\frac{[SO_3]}{[SO_3] + [SO_2]}$$

Then let

$a = \%\ O_2$ in original gas
$b = \%\ SO_2$ in original gas
$100x = \%$ conversion

and Eq. 3 can be algebraically transformed to

$$k = \left(\frac{x}{1 - x}\right)\left(\frac{a - \dfrac{bx}{2}}{100 - \dfrac{bx}{2}}\right)^{-\frac{1}{2}} \qquad \text{(Eq. 5)}$$

From the form of this equation it will be seen that it must be worked backwards. That is, values for a, b, and x can be assumed and the corresponding equilibrium constant computed. Then, from Figure 12, the temperature corresponding to that value of the constant can be read.

In spite of much debate on the subject,[74] it is now accepted as a fact[75] that the equilibrium is the same for every catalyst; the relative "values" of different catalysts lie in their effectiveness in increasing the rate of reaction and hence enabling close approach to equilibrium by means of not unreasonable amounts of catalyst. First-class commercial plants usually attain within 1 or 2% of the equilibrium conversion.

Effect of Temperature on Conversion—Figure 12 was calculated, by the method outlined above, for 7% brimstone-burner gas, i.e., the gas resulting from burning sulfur (not pyrites) in such a quantity of air that the resulting gas contains 7% SO_2 by volume. This gas will contain 13.99% O_2, since 7%

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[73] Miles, loc. cit., p. 100.

[74] Bancroft, Ind. and Eng. Chem., *16,* 645 (1922).

[75] Taylor, G. B., Tenth Report of the Committee on Contact Catalysis, pp. 11-12.

out of the original 20.99% O_2 that air contains has been used to form the SO_2. The effect of high temperature in reducing the possible conversion is clearly shown. However, since the velocity of reaction is with most catalysts about forty times as great at 500° as at 400° C., it is customary to pass the gas first over a very hot portion of the catalyst (above 500°), then over portions at successively lower and lower temperatures (down to 400° or even 375° C.), and thus eventually high equilibrium is approached. Best utilization of the catalyst is obtained by converting about 93% of the SO_2 at temperatures above 500° C. This subject will be amplified later.

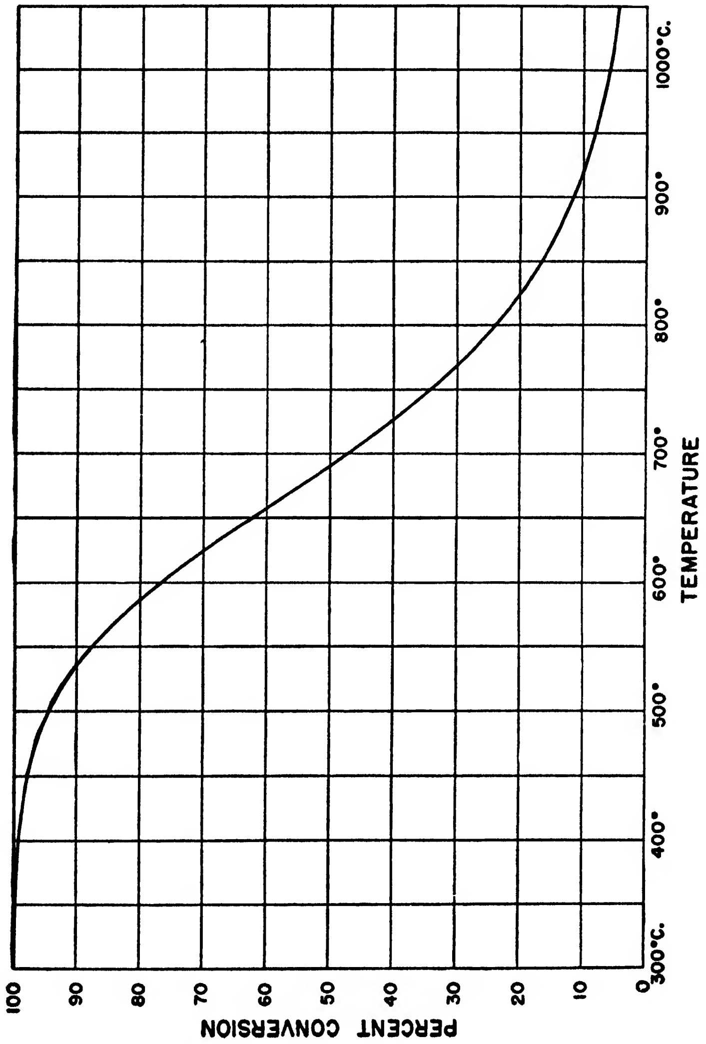

FIG. 12. Equilibrium Conversion for 7 Per Cent Brimstone Burner Gas.

Effect of Gas Strength on the Equilibrium—The solid lines in Figure 13 give the equilibria for those strengths of brimstone-burner gas and those temperatures likely to be encountered in practice. These have been calculated from Figure 12. It will be seen that the possible conversions with weak gas (low SO_2 content) are somewhat greater than with strong. The dash lines give the equilibria, similarly calculated, for mixtures of SO_2 and air; these are higher because of the greater percentage of oxygen.

Gases from a pyrites burner have lower equilibria than brimstone-burner gas of the same SO_2 percentage, because some of their oxygen has been used in oxidizing the iron. For instance, pyrites gas of 7% SO_2 has approximately the same equilibrium curve as brimstone gas of 10% SO_2.

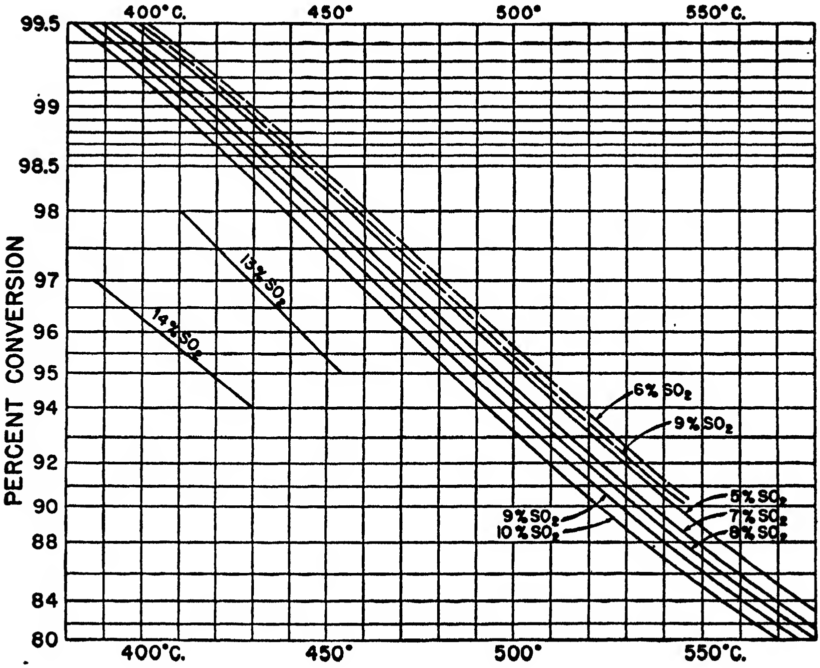

FIG. 13. Equilibrium Conversion for Gases of 5 Per Cent to 14 Per Cent SO_2. The solid lines are for gases produced by burning brimstone in dry air. The upper two lines (dashed) are for artificial mixtures of SO_2 and air.

Optimum Strength of Gas. Computations by means of the reaction-rate equation discussed later in this chapter have been made by the junior author to determine the optimum strength of brimstone-burner gases between 6% and 10% SO_2. These indicate that, to attain equal conversions, the amount of catalyst required per unit of sulfur burned is somewhat less for strong gas than for weak, provided that the conversion required is not higher than a few tenths of a per cent below the equilibrium conversion of the strong gas. For conversions better than this, the weaker gas has the advantage. The reaction-rate equation used in these computations was deduced from various published experiments using platinum catalysts; hence it may not be strictly applicable to vanadium catalysts.

Strong gas, of course, has also the commercial advantage that the volume of gas to be handled for a given amount of acid production is less, hence the gas-handling equipment is smaller and the power costs are less.

Lunge[76] states that the practical maxima are 11.23% SO_2 for brimstone gas, 8.59% for pyrites gas, and 8.12% for gas from "blende" ores. Current practice considers operating maxima to be about 1% SO_2 less than these figures.

The net result of all these considerations is that weak gas (7 to 8%) is desired only where extremely high conversion is preferred to a high rate of production, or where the peculiarities of the plant will not allow strong gas to be handled. The usual stumbling-block in the use of strong gas is insufficient cooling of the interior of the converter.

Kinetics of the Contact Reaction—In an appendix to this chapter there is given a mathematical treatment, based on equations and constants determined from experimental data, of the kinetics of the contact reaction. The general conclusions drawn from this work are given under the five headings below. Literature references are given in the appendix.

Velocity of the Contact Reaction. This reaction, like all catalyses of gases by a solid, includes five steps. Since these steps are consecutive, the slowest one determines the rate of reaction. The steps are:

1. Diffusion of reactants, through the adjacent gas layer, to the catalyst.
2. Adsorption of reactants on the catalyst surface.
3. The chemical change, which occurs at the catalyst surface.
4. Desorption of products of reaction from the catalyst surface.
5. Diffusion of products of reaction away from the catalyst.

The relation of these separate steps to each other is obviously dependent on the physical structure of the catalyst as well as its chemical makeup.

The rate of progress of steps (1), (2), and (3), at any temperature, varies approximately in proportion to the concentration of SO_2 existing at the instant, whereas steps (4) and (5) are slower the greater the concentration. The temperature coefficient (the increase in rate with increase of temperature) of steps (1) and (5) is small, but of (2), (3), and (4) is very large.

The effects of temperature and of concentration on reaction rate may therefore be different with different catalysts and different catalyst-carriers.

Computations of Expected Conversions. The graph of "activity" given in the appendix enables the "specific activity" of any catalyst, at any certain temperature, to be approximately evaluated from a single experimental run (or set of runs at the same flow rate and temperature), provided the experiment is controlled so as to give strictly isothermal conversion. Thus, by a few suitable sets of runs, one can quickly determine: (a) the relative activity of different catalysts, (b) the temperature coefficient of any catalyst, (c) the effect of linear velocity, i.e., the comparison between a broad shallow converter and a narrow deep one, and (d) the conversion to be expected at flow rates different from the one tested.

Effect of Gas-Strength on Conversion. From any one laboratory or commercial run that stops short of equilibrium conversion, Tables 7 to 11 enable

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[76] Lunge, G., "Manufacture of Sulphuric Acid and Alkali," Gurney and Jackson, 1913, Vol. I, Part I, p. 391 ff.

the calculation of what the conversion would have been if the gas had been of a different strength, all other conditions remaining the same. For the tables to be strictly applicable, the runs must be isothermal.

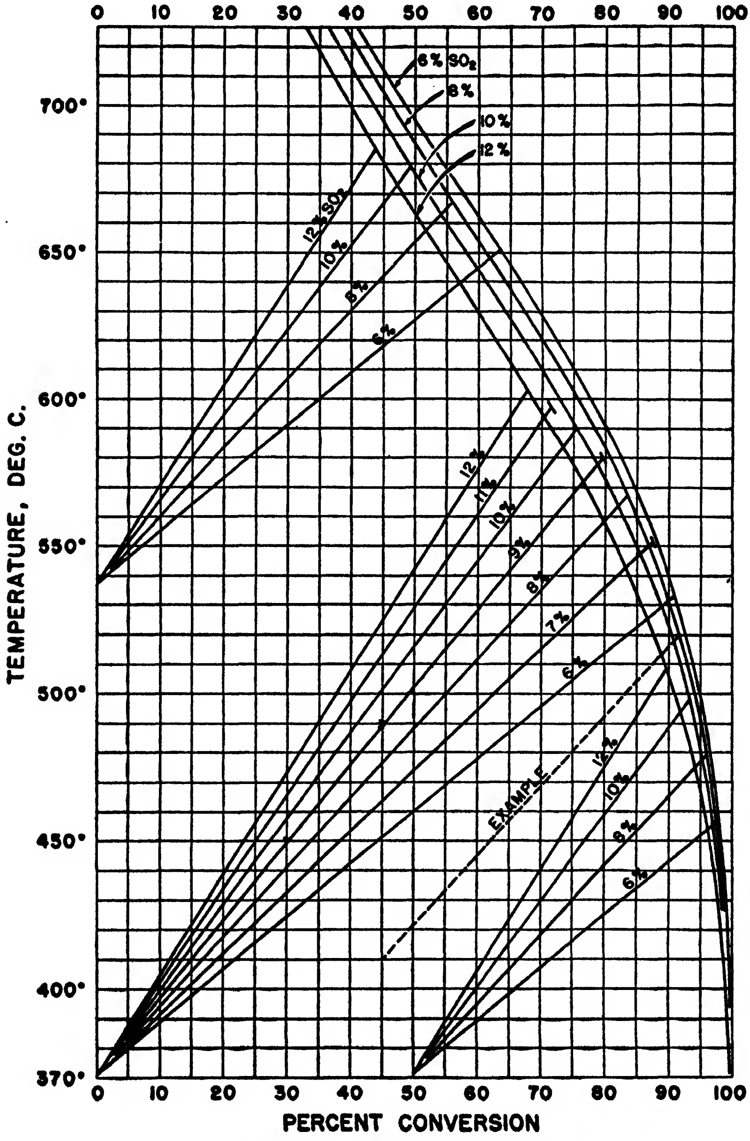

Fig. 14. Temperature Rise Due to Conversion.

SO_2-Air Mixtures vs. Burner-Gas. Laboratory work is often done with gases made by mixing SO_2 with air, hence richer in oxygen than burner-gas. For any one run made with such gas, Tables 12 and 13 enable the calculation of what the conversion would have been with burner-gas of the same SO_2 content.

Temperature Coefficient of the Reaction Rate. Table 14 presents a list of temperature coefficients observed with various catalysts and at various temperatures. It will be seen that, at least up to 475° C., vanadium catalysts have a much greater temperature coefficient than platinum. In practice this is reflected in the lower "ignition temperature" of platinum catalysts.

Temperature Rise Due to the Reaction. The reaction $SO_2 + O = SO_3$ is strongly exothermic. The heat developed at 18° C., according to the International Critical Tables, is 22.2 kilocalories per gram mol of SO_2. At higher temperatures it may be expressed as $22.19 + .000545t$, where t is the centigrade temperature. This expression was formulated from the work of A. P. Beardsley,[76a] which correlated the I. C. T. value with figures calculated from the change of the equilibrium constant with temperature. This calculation followed Bodenstein's method,[76b] but used more recent values for the equilibrium constant. Thus, in the presence of ample catalyst, the reacting gases will rise in temperature until equilibrium is reached. This effect is shown quantitatively in Fig. 14. The sloping lines show the theoretical course of the temperature rise due to conversion, assuming specific heats for air and SO_2 as given in U. S. Bureau of Mines "Technical Paper No. 445," and that the specific heat (per unit weight) of the gas is the same before and after conversion. Other lines may be drawn, approximately parallel to these, noting that the slope is slightly different in the different regions of the chart. The four curves show the equilibria for 6%, 8%, 10%, and 12% brimstone-burner gases, i.e., the maximum attainable conversions at various temperatures. The "example" line shows that 8% gas at 410° C., already 45% converted, will be heated to 480° C. by conversion to 75%, and will reach equilibrium (91.7%) at 520° C. In actual plants, of course, the gases are cooled during the reaction to enable higher conversions to be reached.

TYPES OF CONTACT PLANT

The principal types of contact plants that have been used for making sulfuric acid are: the Badische, the Tentelew, the Mannheim, the Grillo-Schroeder, and the Chemico-brimstone. All except the last will handle either pyrites or brimstone. For pyrites, which produces a dusty and impure gas, the gas-purification system must be much more elaborate than for brimstone, and involves cooling the gas to near atmospheric temperature. By the addition of such a system, the "Chemico" has been adapted to burning sulfide ores. The Tentelew and the Mannheim are now obsolete, and the Grillo-Schroeder is installed only for use on metallurgical gases.

The Badische process cools and washes the gas with acid and passes it through coke filters, heat exchangers, converters containing fluffy platinized asbestos, and towers in which the SO_3 is absorbed in strong sulfuric acid.

The Grillo-Schroeder is similar to the Badische except that the catalyst is platinized magnesium sulfate.

The Tentelew is similar to the Badische except that the gas is filtered dry and washed with caustic soda instead of acid.

[76a] Beardsley, A. P., unpublished work.

[76b] Bodenstein, Zeit. f. Elektrochemie, June 16, 1905, p. 373.

In the Mannheim process, the hot gas is partially converted by an Fe_2O_3 catalyst, cooled, passed through strong acid to absorb the SO_3, filtered, heated, and sent to the final converters containing platinized mats of asbestos rope.

The Chemico, since it does not use pyrites, omits the scrubbing of the gas and thus conserves heat and greatly simplifies the plant. It has other distinctive features which will be described below.

Other processes are also in use at a few plants. The use of silica gel catalysts,[77] non-poisonable by arsenic, simplifies the gas purification. The Chemico converters and Selden mass, with a gas-scrubbing and purifying system including Cottrell precipitators for removing dust and acid mist, are in use on smelter gases. The Montecatini Corp. (Italy) uses a vanadium catalyst and a heat-recuperating converter, the first stage operating at 550° to 600° C., the second at 420°, like the Chemico system.[78]

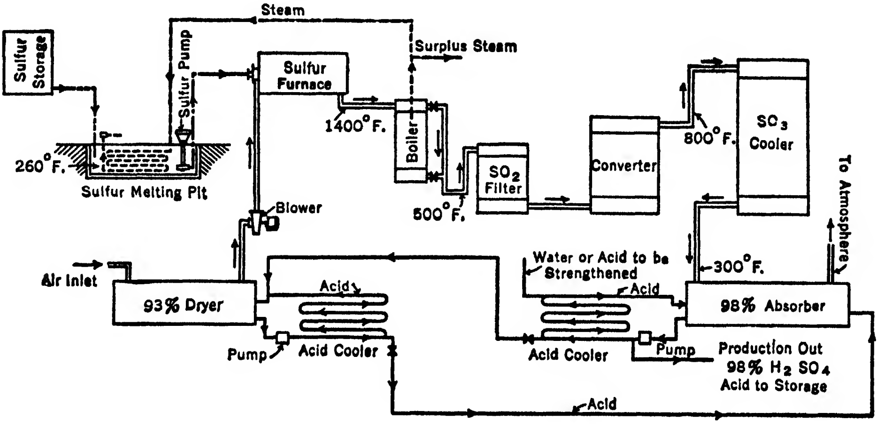

FIG. 15. Flow Diagram, "Chemico" Contact Acid Plant.

The Chemico-Brimstone Process—A flow diagram of a "Chemico" contact-acid plant employing the Selden converter is shown in Figure 15. The sulfur-burning equipment, including steam-heated melting pit, air blower, spray sulfur burner, and waste-heat boiler, has already been described. The air supplied to the burner is usually dried as completely as feasible, in order to avoid formation of H_2SO_4 in the converter. For this purpose it is usually passed through towers fed with acid of 66° Bé. (93%).

To remove dust mechanically carried over, the gas before entering the converter is passed through a filter tower packed with 3″ or 4″ lumps of quartz, since the dust, if carried into the converter, would mechanically clog the catalytic mass. In some late installations this tower is omitted.

The Jaeger Converter. The Jaeger converter system (Figure 16) used in this process takes into account the temperature control required by the thermodynamics of the reaction. The system consists of two layers of catalyst in series, located in one cast-iron converter vessel.

In the first layer, cooling elements consisting of closed-end tubes, each with

[77] Fairlie, loc. cit., pp. 396, 542.

[78] Chem. Abs., *32*, 5163; Cornelio, E., Chimica e Industria *20*, 8-12 (1938).

an open-end tube inside it, are embedded as shown in Figure 16. The incoming gas flows up through the inner tubes and down through the annular space between the tubes, then enters a shallow layer of crushed quartz beneath the catalyst mass and so up through the mass. The mass is thus cooled through its entire depth by the incoming gas. If there were no resistance to heat transfer, this part of the converter would be perfectly self-regulating in temperature against fluctuations in gas flow, because the amount of cooling-medium (viz., the incoming gas) is always in direct ratio to the total heat developed by the reaction. Calculations by the junior author indicate that true radiation[79] accounts for 90 or 95% of the heat transfer from the mass to the outer pipe, and for most of the transfer from the outer pipe to the inner. Since heat transfer by radiation between two bodies is proportional to the difference of the fourth powers of the absolute temperatures of the bodies, any slight increase in the mass temperature would cause a considerable increase in the heat transfer to the metal of the tubes. The heat transfer from the metal of the tubes to the gas takes place partly by radiation, SO_2 being a radiating gas. Such part of the transfer as is due to convection is proportional to the 0.8 power of the gas velocity; therefore, this step of the transfer will nearly keep pace with variations in quantity of incoming gas. Thus it is claimed that an automatic temperature control is obtained without skilled supervision.

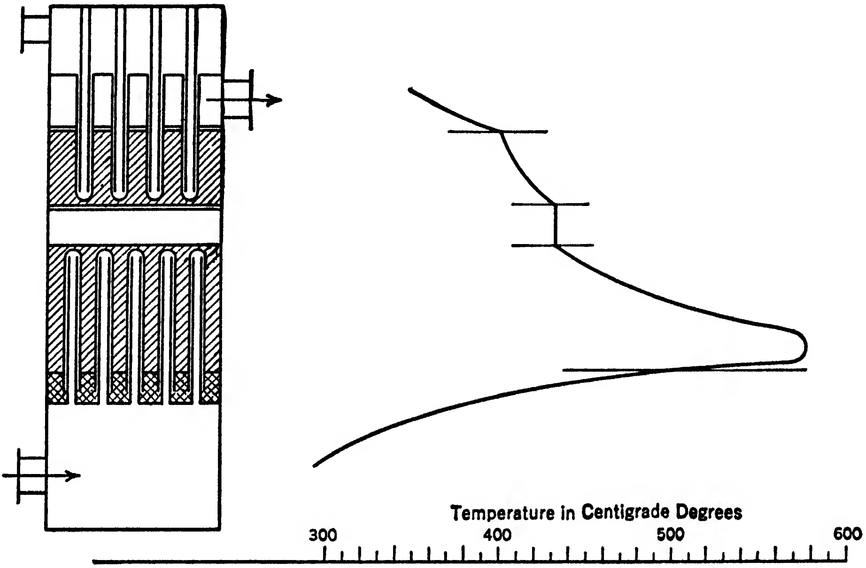

Fig. 16. The Jaeger Converter.

The proportion of reaction gas flowing through the cooling elements is varied from the periphery toward the center in such a way as to compensate for the unavoidable cooling due to the external heat loss from the converter

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[79] For a discussion of heat transfer by radiation see Chapter 2.

shell; thus a more uniform temperature is maintained throughout each horizontal cross-section, a distinctive feature of this type of converter.

The second layer of catalyst is provided with similar cooling elements; these utilize cold air. Thus a lower temperature (430° to 400° C.) is obtained, desirable to give a high equilibrium conversion in this the final section of the converter.

The graph in Figure 16 shows approximately the course of the temperature of the gas as it passes through the converter, leaving the mass at 400°, at which temperature a conversion of 99.33% is theoretically possible with 8% gas. Incidentally, the gas is shown as being further cooled to 350° after leaving the mass. As shown in Figure 17, about 96% conversion out of a total of 98% occurs in the first layer of the catalyst. Nevertheless, in the second layer, because of the great decrease in reaction velocity caused by the lower temperature as well as by the nearness to equilibrium, a longer period of contact with the catalyst is required. The larger cross-section of catalyst in the second layer resulting from the less close placement of cooling elements (less cooling being required) assists in achieving this. Figure 17 is a presentation of the course of temperature and conversion that the design of this converter aims to accomplish. If we were to draw on this diagram a graph of equilibrium conversions corresponding to the temperatures given, we would find that by the time the gas has passed 25% of the catalyst it has reached the equilibrium (89%) for the temperature existing at that point, hence no more conversion is possible without cooling. We further find that, upon cooling, the gap between obtained conversion and equilibrium increases to 3% at

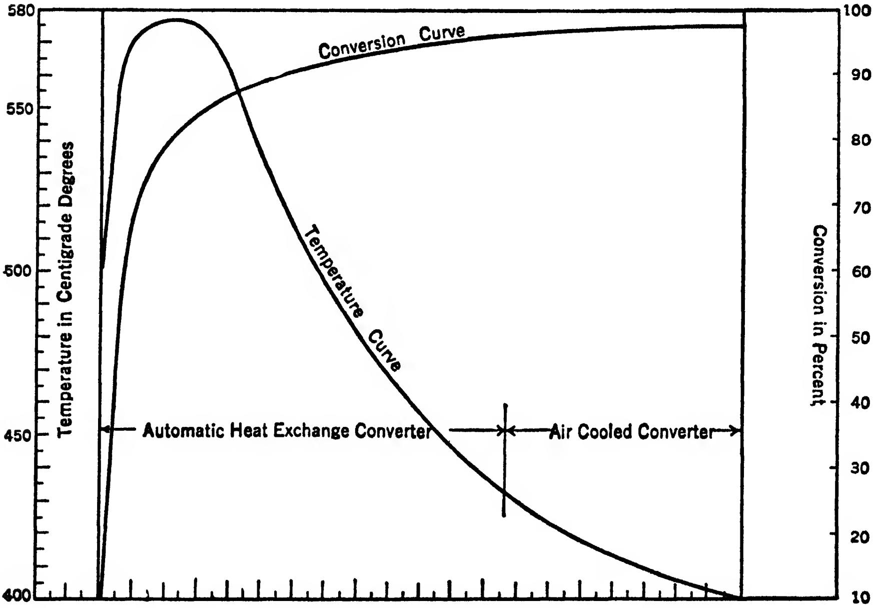

Fig. 17. Ideal Temperature Distribution in Converter.

the halfway point of travel, then decreases to about 1¼% at the conveyor exit. Obviously, an increase in the amount of cooling air used would tend to increase this gap and so increase the reaction velocity; on the other hand it would, by the action of the temperature coefficient, tend to decrease the reaction velocity. Thus there is an optimum air flow for any given conditions, which can be predicted approximately by calculation and determined finally by trial.

The converters are built in various sizes up to a capacity of 70 tons H_2SO_4 per day. The 40-ton size is 10½ feet diameter and 16 feet high. For an 80-ton or 120-ton plant two or three 40-ton converters are connected for parallel operation from one sulfur furnace with one set of absorbing towers.

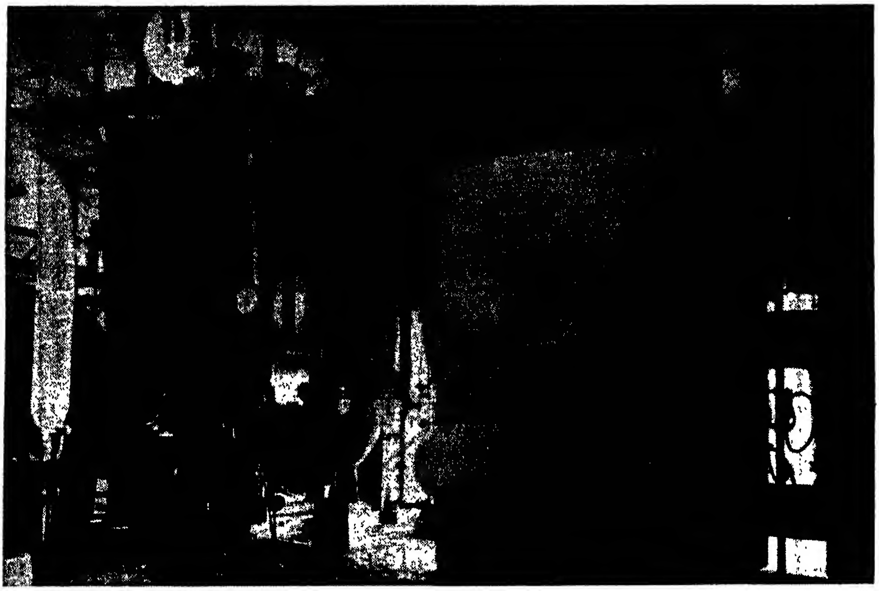

Fig. 18. Jaeger (Selden) Converter; Waste-heat Boiler in Background.

Cooling and Absorbing the SO_3 Gas. From the converter, the oxidized gas is cooled to about 150° C. in steel multi-tubular coolers. It then passes to one or more packed towers (Figure 19), where it is absorbed in acid. These towers can be so designed and controlled as to give acid or oleum of any desired strength. The operation and control of absorbing towers, and the methods of obtaining acids of various strengths, are practically the same for all the various sorts of contact plants; this will be described later under the headings "Cooling the SO_3 Gas" and "Absorbing the SO_3 Gas."

Control. The plant is controlled from one central room which contains the recording and indicating pyrometers, SO_2 gas-analyzing apparatus, etc. Figure 20 shows a typical control room. The left-hand instrument is a multipoint recorder which by means of electrolytic cells records the strengths of the acids flowing in various parts of the plant. The two other multipoint instruments record gas temperatures in the converters and elsewhere. The large indicator shows the temperature of the sulfur furnace. The small indicating instruments, by means of the switchboard, can be instantly connected to any chosen thermocouples out of a number permanently installed in various spots about the plant. The SO_2 analyses are performed on the bench at the right. In some plants continuous SO_2 indicators and controllers have been installed; these operate by measuring the thermal conductivity of the gas flowing through sampling chambers, but have not been completely successful in practice.

Fig. 19. Absorption and Drying Towers; Plant for 75 Tons H_2SO_4 per day.

Fig. 20. Control Room of Chemico-Brimstone Plant.

This centralized control results in a saving of labor so that only one or two operators and a helper for wheeling sulfur, oiling machines, etc., are required per shift. Less ground space is required than for the older types of contact-acid plants and far less than chamber plants of equivalent capacity.

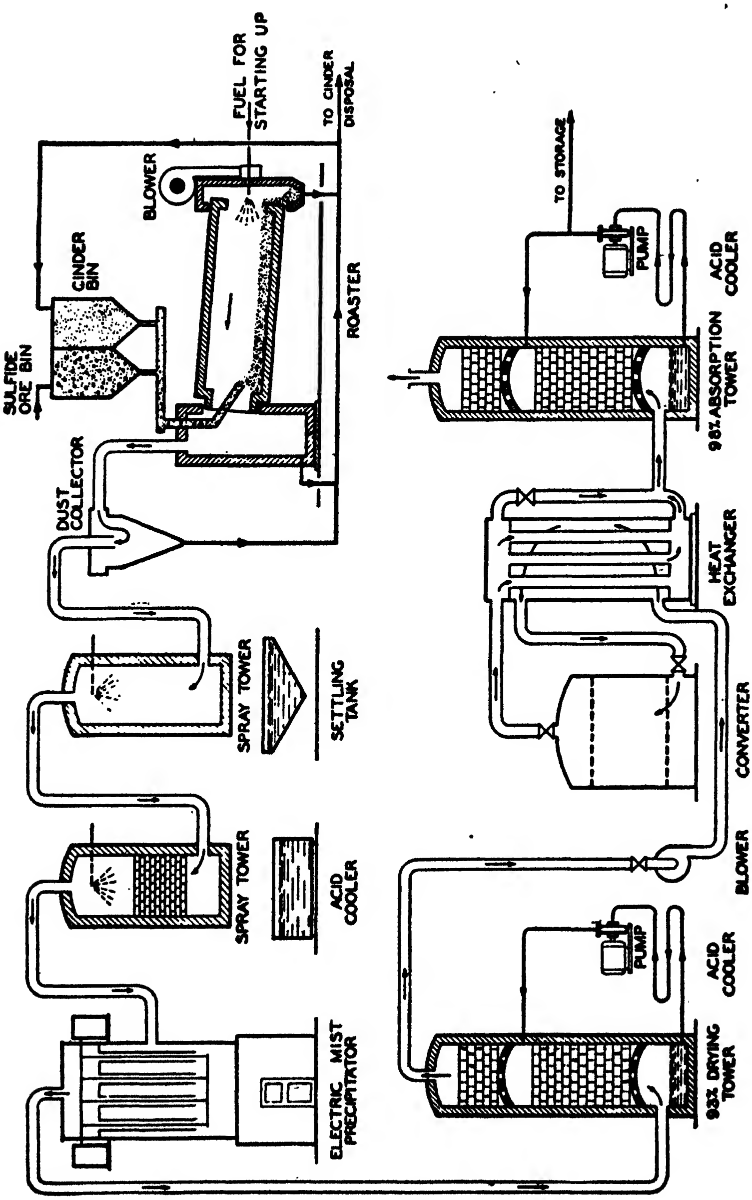

FIG. 21. "Chemico" Sulfuric Acid Contact Process (Using Sulfide Ore). (Courtesy Chemical Construction Corp., New York)

The Chemico Process for Pyrites or Smelter Gases—If pyrites ore or smelter gases are used as the raw material, they must be freed of suspended solids to avoid mechanically clogging the catalyst and contaminating the acid produced, not because of any danger of chemically poisoning the vanadium catalyst. Figure 21 shows the Chemico system of accomplishing this. To remove the suspended solids, the gases are passed through a cyclone dust-collector and then scrubbed with weak acid in a series of two towers. Next the gases are freed of acid mist by a Cottrell electrostatic precipitator, and finally dried in a packed tower by 93% acid. By these processes the gases are cooled below the proper temperature for admission to the converter. They are then heated in a heat exchanger by the heat of the gases leaving the converter. Commercial plants using Selden mass and converters are in operation on such gases, and are producing a pure, clear acid with the same conversion efficiencies obtained in sulfur-burning plants.

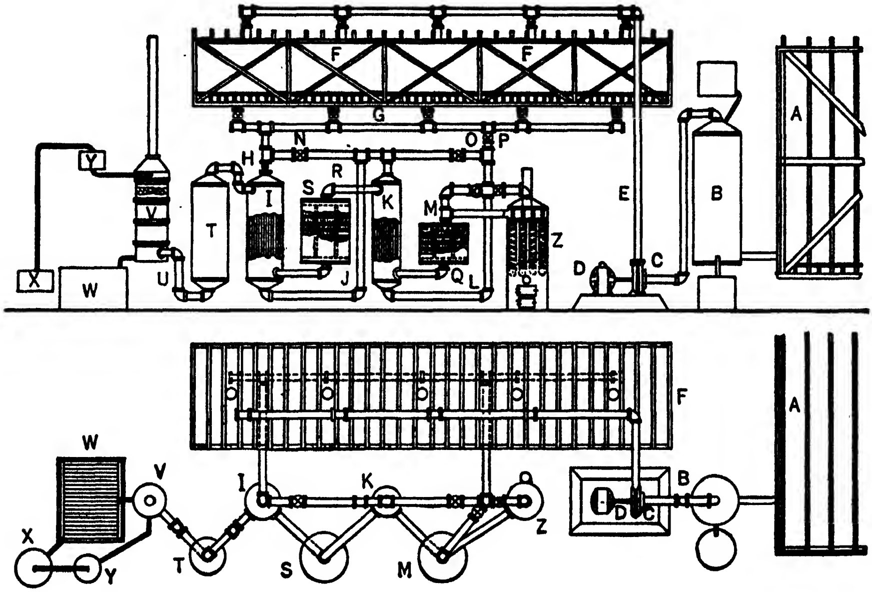

FIG. 22. Diagram of Badische Process.

The Badische Process—There were few installations of the original Badische process. Litigation over the United States process patents led to a settlement between the parties involved, and the General Chemical Co. acquired the rights in the United States, but its plants, which had been built prior to the litigation, were not altered substantially after the settlement, as they had been developed independently to a rather high state of perfection. A schematic diagram of the General Chemical Co. form of installation is shown in Figure 22.

Cooling the Gas. In Figure 22, A is a preliminary cooling and dust-separating apparatus into which the hot burner-gas and steam are admitted and allowed to cool slowly. An old "chamber-process" chamber, into the first part of which some steam is injected, may be used. In this case steam is desirable rather than water, because the incipient condensation of water on the minute suspended dust particles coagulates the particles and hastens their deposition. Condensation on the walls keeps them free from dust and improves the heat-transmission coefficient.

Instead of this wet-wall chamber cooler, a dry cooler consisting simply of cast-iron pipes exposed to the atmosphere may be used. In some plants these pipes are enclosed, forming a heat exchanger to heat the cold purified gas going to the converters. In either case the dry cooler may be followed by a Cottrell for electrostatic precipitation of dust.

The hot gas always contains a little SO_3 formed by the catalytic action of the rusty iron surfaces in the burner and elsewhere, also some water which enters with the sulfur as well as in the atmospheric air. Therefore, it must not be cooled to its dewpoint in iron pipes, for if it is, the condensed acid will corrode the iron and may form arsine with any As_2O_5 present, causing poisoning of the catalyst. The dewpoint of the gas is of course higher the more water it contains; a rough rule is to keep the gas above 275° C. while in iron.

Scrubbing and Drying the Gas. The gas must be fairly well dried before entering the converters, to avoid the deposition of sulfuric acid therein and also the corrosion of iron pipes and apparatus. Sulfuric acid will ruin a vanadium catalyst by forming sulfates. A moisture content of 3 to 6 mg. per cu. ft. is considered good practice, though Miles[80] prefers 0.6 to 2.0 mg. per cu. ft. (.02 to .07 gm. per cu. meter). However, a slight amount of moisture is necessary for effective conversion by platinum catalysts Russel and Smith[81] have shown in the laboratory that if the gases are dried over P_2O_5, practically no conversion occurs.

For drying and scrubbing the gas, one or more washers or scrubbing towers *B,* fed with strong sulfuric acid, are used. In most plants, these have steel shells and are designed for acid of 92 to 98%.[82] However, if the gas should remain in contact with acid of this strength for sufficient time to come to equilibrium therewith, its moisture content would be reduced to about .02 mg. per cu. ft. The amount of acid must therefore be controlled so as not to overdry the gas.

Another method, employed by the senior author, is to use large towers and a liberal quantity of 80% (61° Bé.) acid. Gas brought to equilibrium with such acid will still contain about 6 mg. of water per cu. ft., therefore no control of acid quantity is needed. These towers are of acid-proof construction, lined with brick and filled with a packing of acid-proof shapes or quartz. They may have either steel or lead shells. For 80% (61° Bé.) acid, the latter are more durable, although steel shells carefully protected by tight brick linings will last for years. The towers are equipped with ample coolers for the acid. As the acid is used over and over again, it becomes weaker by the amount of water removed from the gas, and must be strengthened by adding stronger acid from the SO_3 absorbers.

The towers also remove the residual dust and most of the arsenic oxide. For the removal of special impurities that occur in certain gases, such as

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[80] Miles, loc. cit., p. 241.

[81] J. Chem. Soc. (London), Trans. 77, 340 (1900).

[82] Fairlie, loc. cit., p. 352.

fluorine, chlorine or hydrochloric acid, weaker acids may be used in the first tower.[83]

Coke Filters. The gas is now picked up by the blower *C*, capable of forcing the desired volume of gas against a pressure of 5 to 8″ of mercury. Most of this pressure is friction through the coke filters. The blower is driven by a motor *D*.

With most ores, the gases are at this stage free from nearly all impurities except impalpable dust, entrained particles of acid from the washers, and the fume of H_2SO_4 formed by condensation. These particles and fume contain considerable arsenic oxide if there was any in the gas. The flue *E* carries the gas over to the bank of filters *F* built on the Kessler principle, i.e., slow, even filtration through a large cross-section. These contain crushed coke carefully sized and free from dust. The first layers consist of 4″ lumps carefully laid by hand; on these is placed a 6″ layer of sizes graduated to ¼″, then finer coke for a depth of several feet, grading down in size to about 1 mm. The area usually provided is 1 sq. ft. for every 85 cu. ft. of gas per hour. Downward circulation is best, so that when cleaning any one filter its top surface only need be stripped and replaced with an equal quantity of fresh coke. When the gas is purified as fully as possible in the towers, such renewals are infrequent; their necessity is indicated by the stoppage of the draft. If the filters are working properly, a concentrated pencil of light of the intensity of direct sunlight is entirely invisible (Tyndall's test) when thrown through the gas before entering the contact mass.

Heat Exchangers and Converters. From the filters *F* the gas is collected into the pipe *G*, which carries it over to a tee where it may be routed in either of two directions by the valves *H* and *N*. The greater portion of the gas passes downward through the inner tubes of the heat exchanger *I*, and thence via the pipe *J* through the inner pipes of a second heat exchanger *K*. Valves *N*, *O*, and *P* are provided for regulating the temperature of the contact mass in either converter by admitting a portion of the unheated gas. By the valve *N*, gas may be taken directly into the second heat exchanger *K*, and likewise partially heated gas may be taken from the first heat exchanger *I* directly into the first converter *M*, if desired.

From the second exchanger *K*, the gas normally passes through the pipe *L* over and down into the first converter *M*. Entering this converter it is expected to have a temperature approaching 400° C. and in this converter, which may be shorter than the other, about 80 to 85% of the conversion is expected to be carried out. Theoretically, 8% gas entering at 400° C. a converter of ample capacity and perfectly insulated against heat loss by radiation would eventually attain a temperature of 587° C. and a conversion (equilibrium) of 79%. Loss of heat by radiation to the atmosphere lowers the temperature and consequently raises the equilibrium conversion and so enables greater conversion.

Leaving the converter at the bottom through the pipe *Q*, the gas passes across outside the pipes in the heat exchanger *K* and down through the pipe *R* into the second converter *S*. The second converter is made larger than the

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[83] Fairlie, loc. cit., p. 345.

first, and carries much more, and sometimes richer, platinized asbestos; this is required because the reaction is slowed by the low temperature and the closeness to equilibrium. In this converter, an additional conversion of 15% will raise the temperature of the gases 35.5° C. (disregarding loss by radiation); therefore, if the gases are cooled to 400° or 420° by the heat exchanger *K*, they will not rise in the second converter *S* to a temperature so high as to prevent obtaining a satisfactory total conversion. Extremely careful regulation of the temperature is maintained at the entrance and various other points in the first converter.

Each converter consists essentially of a vertical cylindrical shell divided into a number of superposed chambers by perforated cast-iron shelves. On each shelf is spread a layer of platinized asbestos. In some designs there are as many as 50 shelves, spaced 1″ apart and each carrying ½ to ¾″ of asbestos; in others only a few shelves are used, with deep layers of asbestos. The gas passes from chamber to chamber through the asbestos, travelling downward to avoid lifting the asbestos. The advantages of the multi-shelf converter are that it distributes the gas and mixes it thoroughly, also that the danger of compacting a thick layer of asbestos is avoided. The disadvantage is the cost of constructing and filling, and especially the time required to refill it in case of damage by poisoning.

The coal-fired heater *Z* is required when starting the plant, to heat the gas and thereby bring the contact material to the ignition point. It may be located anywhere along the pipe line *H N P O L*. It is provided with valves and connections so arranged that the gas may be by-passed through it at any time during the process when it is necessary to maintain a higher inlet temperature at the first converter.

Absorption of SO_3. From the second converter the gas passes to the first exchanger *I*, giving up the greater portion of its heat by heating the entering gas.

A water cooler or, in recent practice, a tubular air cooler *T* is required to bring the temperature of the gas down to the point (150° C.) where the SO_3 can be satisfactorily absorbed. The cooled gas leaves by the pipe *U* and passes up the absorbing tower *V*, where it meets a stream of 98.5 to 99% acid at 50° to 80° C. flowing down over the loose acid-proof packing of the tower.

Production of Acid. The acid from the bottom of the tower passes into the cooler *W*, from which is drawn the acid for sale. The waste gases from this tower go to the atmosphere. Sufficient acid for the circulation is run into the tank *X*; a centrifugal pump lifts this to the feed tank *Y*, whence it flows by gravity to the tower *V*. Water (or weak acid from some other source such as a chamber plant) is added to the circulation, to make up for the acid withdrawn and so keep the circulating acid at the proper strength. The control and operation of the SO_3 coolers and absorbers will be described later.

Costs. Little or no fuel need be used for the operation of the system. The actual cost of manufacture per 100 lbs. of H_2SO_4 as 98% acid is sometimes even less than the cost of making 100 lbs. of H_2SO_4 as 52° Bé. (65%) chamber acid at the same location, with the same price of ore and the same labor conditions. Repairs compare favorably with the chamber plant.

Two units like the one illustrated in Figure 18, i.e., a so-called double unit, have a capacity of about 25 tons of 100% H_2SO_4 per day, and cost about $175,000.

The Grillo-Schroeder Process—The most widely used platinum contact-process system in the United States has been the Grillo-Schroeder, Figure 23, which has been built in a number of ways. The various modifications are in design of the plant, rather than method. Much the same steps are, in general, employed in all the modifications.

The plant shown in Figure 23, like the large U. S. government plants built during the World War of 1914-18, was designed without regard for heat economy. These plants were in locations where natural gas was cheap, and in view of the extreme haste, simple gas-fired heaters were preferred to the more costly heat exchangers with their complications of piping.

Cooling, scrubbing, and drying the gas can be done exactly as described for the Badische process. However, in the plant illustrated, the gas first passes through a tower fed with a heavy stream of 60° Bé. (78%) acid, then through lead pipes cooled externally by water, and finally through another similar tower with 60° Bé. acid.

Coke Filters. A steel- or lead-pipe line carries the gas to a coke filter similar to the Badische type, then through "fine filters," which are usually made of cast iron and have layers of asbestos fibre or mineral wool. The gas from these filters is cool and free from dust and from most impurities, but still contains a little moisture unless 93 to 98% acid was used in the second tower. This moisture may now be removed in a final drying tower where the gas is scrubbed with 93 to 98% acid. This tower may form a little mist, so the gas is passed through another coke filter to remove it.

Gas Heater. The gas is moved through the entire system by means of a positive-pressure blower located beyond this second coke filter. The gas is forced through a preheater in order to raise its temperature to the proper "ignition" point to initiate conversion by the catalyst, i.e., 380° to 400° C. The preheater in these government plants was a furnace fired with gas, containing cast-iron pipes through which the gas passes. In plants designed for heat economy this heating is done by heat exchange from the burner-gas.

Converters. The usual Grillo-Schroeder converter is made of cast iron or steel and has 5 or 6 trays on each of which is placed a layer of contact mass 9 to 12″ deep. The mass is platinized magnesium sulfate in about ½″ lumps. Its preparation has already been described. The arrangement is similar to the Badische converter already described, but the gas passes upward. It will be obvious that in the plant illustrated the converters must be of recuperative design (i.e., self-cooled by the incoming gas), otherwise overheating and poor conversion would result. The converted gas (SO_3) is cooled and absorbed as in other plants.

Cooling the SO_3 Gas. The treatment of the oxidized (SO_3-bearing) gas to form acid or oleum of any desired strength is essentially the same in any type of contact plant. The SO_3 leaving the final converter passes through the tubes of a steel multi-tubular cooler in which cold air is blown over the outsides of the tubes. In modern practice the SO_3 gas is thus cooled to 150° C.

or somewhat less, and is then sent to the absorbing towers. Older practice in platinum-catalyst plants was to cool the gas further, to 40° C., in a water-cooled apparatus before sending it to the absorbers; some years later 70° was customary. Oleums of 40 to 45% SO_3 freeze at about 35° C.; therefore, at this temperature or below, the pipes may become clogged. On the other hand,

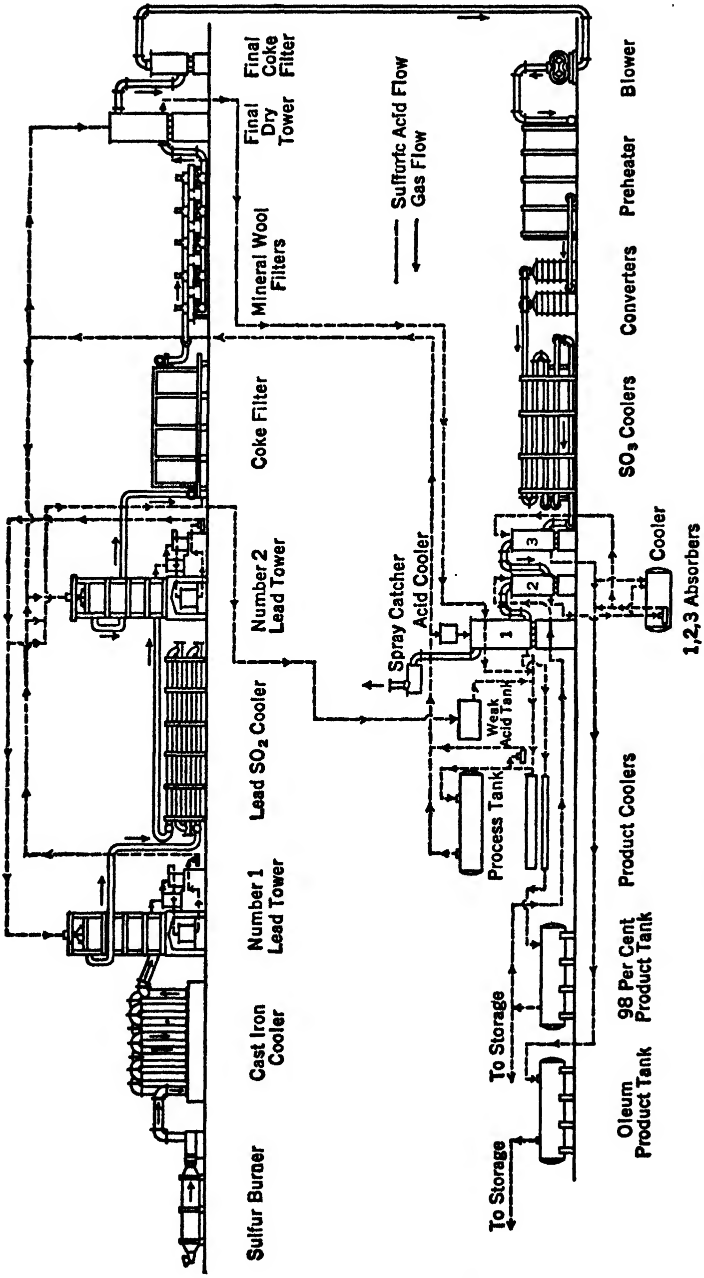

FIG. 23. Diagram of Grillo-Schroeder Process.

if the gas be sent too hot to the absorbing towers, contact with the acid therein forms a mist of H_2SO_4 which passes unabsorbed through the towers and escapes to the atmosphere. Excessively hot gas also heats the acid to such a point that corrosion of the tower and piping becomes appreciable.

Absorbing the SO_3 Gas—*Making 98.5% Acid.* Whenever SO_3 gas is brought into contact with water vapor, a fog of exceedingly fine droplets of H_2SO_4 is formed. This fog, once formed, is very persistent; it is practically impossible to remove it from the gas by any form of washing or absorbing tower. To absorb SO_3 from gas, therefore, one should use acid strong enough and cool enough to have little or no water vapor over it, i.e., 98% or stronger. On the other hand, if the absorbing acid in the final tower has any appreciable partial pressure of SO_3, just that much SO_3 will be lost in the waste gases passing out of the tower; this acid should therefore not be much stronger than 99% without special cooling. These considerations thus dictate a strength of 98.5% for the acid in the final absorbing tower, and modern practice adheres closely to this. If the plant is designed to make only 98.5% acid, therefore, one absorbing tower is all that is needed.

Making Oleum. If oleum is to be made, the gas must pass through at least two absorbing towers, first one in which oleum is circulating, then one in which 98.5% acid is used. The water or dilute acid required is added at the 98.5% tower, and the "make" or increment of acid from addition and absorption in this tower flows to the oleum tower. Since oleum absorbs SO_3 rather slowly, the two-tower system is not sufficient for making oleum stronger than 20% (i.e., oleum containing 20% free SO_3).

For 30 or 35% oleum (and not infrequently for 20%), three or more absorbing towers are used. They may all be arranged in series, the "make" of acid passing from one to another (counter-current to the gas) as it is strengthened. Not infrequently the two towers nearest the converter are operated in parallel, especially if there are four or more towers in the train.

It is possible to make 40% oleum in this way if the oleum tower is well cooled. Since oleum of this strength freezes at 35° C., it is only manufactured for purposes for which no other strength will answer. It is made principally by explosives manufacturers, who for their own use can mix it with nitric acid before cooling; this prevents freezing.

Construction of Absorbing Towers. The absorbing towers are usually of steel plate with a lining of 2½ to 4" of acid-proof brick. For a 120-ton Chemico plant they would be 11 feet in diameter and 28 feet high. They are filled with a packing of small stoneware "spiral rings" or other blocks shaped especially to expose a great surface;[84] formerly, lumps of quartz or coke were used.

Though not shown in Figures 13, 20 or 21, it is not unusual to pass the gas from the final acid-circulating absorption tower through another tower similar except that it is run dry, i.e., without any acid. This tower serves to remove mist from the gas. The waste gas then carries away practically no SO_3, but contains of course the unconverted SO_2; e.g., if the burner-gas was 8% SO_2 and conversion was 97%, the exit gas would contain 0.24% SO_2.

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[84] Fairlie, loc. cit., p. 228.

Distillation for Strong Oleum—To produce oleum of 66% SO_3, such as is required for sulfonation in the manufacture of dyes and intermediates,[85] a direct-fired steel still, having a condenser and receiver of steel, is used. The still is charged with oleum of 20 to 30% free SO_3. A layer of similar oleum is placed in the receiver and kept thoroughly cooled and stirred during the distillation. When the desired strength of oleum is obtained in the receiver, the distillation is stopped. The residue in the still is weak oleum and may be returned to the contact plant absorbers.

Purity of Contact Acid—Whenever acid of a high degree of purity and water-white color is required, there is no doubt as to the superiority of the contact process. Only by expensive distillation can ordinary sulfuric acid be purified to be comparable with the usual contact acid.

THE CHAMBER PROCESS OF MANUFACTURE

History—In 1746, Dr. Roebuck constructed a lead chamber for the manufacture of sulfuric acid by an intermittent process. Steam was first used in the chamber in 1774; air was admitted continuously for the first time in 1793. Progress was rapid after the invention of "lead burning" (welding) in 1838. The Gay-Lussac tower for the recovery of oxides of nitrogen was invented in 1827, but was not put into practice till 1842; even up to 1867 the majority of plants were not using it. The Glover tower, for de-nitration, was first built in 1859 and was generally adopted by 1870. Modern developments have been chiefly concerned with certain improvements for reduction of costs, such as more effective methods of cooling the chambers which enable a reduction in their size. Otherwise the process has not changed much since 1870.

General Description of Process—Clear understanding of the chamber plant is more easily obtained by first considering the general method of carrying out the process and then noting modifications of process and of apparatus that are made in practice at one point or another. The basis of all chamber plants, no matter how modified, is that, in a mixture of sulfur dioxide and water vapor in proper proportions and at suitable temperature, the presence of certain oxides of nitrogen (collectively referred to as "niter") causes the oxidation of SO_2 to SO_3; the latter then combines with water to form H_2SO_4.

Chemistry of the Chamber Process—The chamber process might be classified as catalytic inasmuch as the oxides of nitrogen which are required to cause the formation of $2H_2SO_4$ from $2SO_2 + O_2 + 2H_2O$ are not present in the finished product. However, it is perhaps more exact to consider it as a cycle of several successive chemical reactions. In the history of the process, several theories have been propounded as to what the intermediate reactions are.

Lunge's original theory[86, 87] is still sound in principle, though now believed to give only a part of the picture. He stated that the intermediate product was nitrosylsulfuric acid (SO_5NH or $SO_2 \cdot OH \cdot ONO$ or $HSO_3 \cdot NO_2$). The "chamber crystals" sometimes found in the chambers (when the water supply is insufficient) have this composition.

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[85] See Chapter 28.

[86] J. Chem. Soc., *47,* 470 (1885).

[87] Berichte, *21,* 67, 3323 (1888).

Lunge and Ernst Berl[88] later announced an intermediate product between SO_2 and SO_5NH. This they called sulfonitronic acid, SO_5NH_2. Since it is violet-blue in color it is now commonly called "violet acid"; its formula is sometimes written $H_2SO_4 \cdot NO$ or $H_2SO_3 \cdot NO_2$.

In 1935, E. Berl,[89, 90] as a result of further research directed toward high-pressure synthesis of sulfuric acid, further modified the reactions, as follows:

(1) $2NO + O_2 \rightarrow 2NO_2$ .... In the gas phase
(2) $SO_2 + H_2O \rightarrow H_2SO_3$ .... On the gas-liquid surface
(3) $H_2SO_3 + NO_2 \rightarrow (H_2SO_4)NO$ .... "
(4a) $2(H_2SO_4)NO + \frac{1}{2} O_2 + (NO_2) \rightarrow 2SO_5NH + H_2O(NO)$ "
(5a) $2SO_5NH + SO_2 + 2H_2O \rightleftarrows 2(H_2SO_4) \cdot NO + H_2SO_4$ ..... "
(4b) $(H_2SO_4)NO \rightleftarrows H_2SO_4 + NO$ .... In the liquid phase
(5b) $2SO_5NH + H_2O \rightleftarrows 2H_2SO_4 + NO + NO_2$ .... "
(5c) $SO_5NH + HNO_3 \rightleftarrows H_2SO_4 + 2NO_2$ .... "

Oxygen, by equation (1), rapidly converts NO (colorless gas) to NO_2 (actually N_2O_4, red gas). In the presence of small amounts of SO_2, as at the chamber exit, the reaction stops at 50% completion, so that the oxides of nitrogen at this point can be regarded as N_2O_3.

Equations (2), (3), (4a) and (5a) show the production of H_2SO_4 on wetted surfaces, with formation and decomposition of violet acid and nitrosylsulfuric acid successively.

In the body of the liquid, the same results are obtained via equations (2), (3), (4b), (5b) and (5c). Violet acid decomposes completely, by equation (4b), in sulfuric acid of 50% strength or less, but is quite stable in acid of 80% or stronger.

GENERAL DESCRIPTION OF A CHAMBER PLANT

Although the chamber process evolved by the slow methods of trial and error long before the fundamental chemistry was known, the steps involved make up a logical and simple procedure for carrying out the various reactions.

The three essential parts of the plant, after the burners, are: the Glover tower, the chambers, and the Gay-Lussac tower.

The process comprises six steps:

1. Sulfur dioxide gas is produced by combustion of sulfur or sulfides.

2. "Oxides of nitrogen" (NO and N_2O_4) are made, usually by catalytic oxidation of ammonia.

3. The hot burner-gas passes up through a "Glover tower" down which is flowing the "nitrous vitriol" produced in Step 5. The hot gas drives out the oxides of nitrogen from the vitriol, and is cooled. Some oxidation of SO_2, and consequent formation of H_2SO_4, also occurs.

4. The gas and the nitrous oxides obtained from Steps 2 and 3 enter the "chambers," where steam and water are added and sulfuric acid of 50° to 54° Bé. (62 to 68%) is formed by oxidation and hydration of the SO_2.

5. The residual gas passes up through the "Gay-Lussac towers," down which flows cool 60° Bé. (78%) sulfuric acid; in this cool acid the oxides of nitrogen are soluble and so are absorbed, forming "nitrous vitriol."

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[88] Z. Angew. Chem., *19,* 807-819; 857-869; 881-894 (1906).
[89] Trans. Amer. Inst. Chem. Eng., *31,* 193 (1935).
[90] Chem. and Met. Eng., *41,* 571 (1934).

6. The 50° acid formed in Step 4, unless sold as such, flows down the "Glover tower" of Step 3, as does also the nitrous vitriol; it is thus partly concentrated, and forms acid of 60° Bé. (the final product of the plant) while the nitrous gases return to the cycle.

Flow of the Gas—The general arrangement, in plan and in elevation, of a conventional chamber plant is shown in Figure 24. From the burner dust-catcher (1) the gas is forced by the blower (2) up through the packed Glover tower (3). In some plants the blower comes after the Glover as shown at (4); sometimes it is assisted by another blower (12) later in the process.

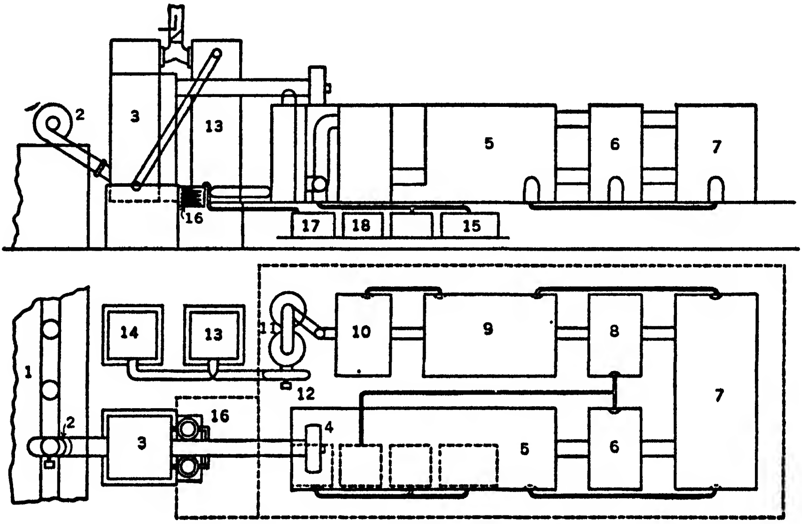

Fig. 24. Arrangement of a Chamber Plant.

Next the gas passes in series through three or more "lead chambers" (5), (7), (9). The gas contains some water evaporated out of the acid in the Glover tower, and water is sprayed into the chambers; thus liquid acid is formed in the chamber by cooling and condensation, both on the walls and as a mist or rain in the body of the chamber. The chambers are simply large rooms whose walls are of sheet lead hung from a steel or wooden framework. Originally these chambers were of enormous size; but it was later discovered that the principal value of the large size was in dissipating to the atmosphere the heat of the reaction ($SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow H_2SO_4 + 54{,}000$ calories, i.e., approximately 1000 BTU per pound of H_2SO_4) and thus that smaller chambers would suffice if externally cooled, as by water flowing over them.

Some large plants, to assist in cooling and mixing the gases, interpose towers (6), (8), (10), the gases passing through a tower after leaving each chamber. The towers may be empty or, better, packed with lumps of quartz or ceramic shapes. Cold water or dilute acid is fed in at the top, cooling the gases and supplying H_2O for the further formation of acid.

The modern tendency is to use more and smaller chambers, so as to increase the mixing effect and to increase the inside surface for reaction and the outside surface for cooling.

The SO_2 is now practically completely reacted to H_2SO_4. Next comes a cooling device consisting of either towers (11) or a long flue.

Next the gases pass up through the Gay-Lussac tower or towers, usually two in series, (13) and (14). In these the down-flowing acid dissolves and abstracts nearly all the nitrogen oxides from the gases. From the last tower the gases are discharged into the atmosphere.

Flow of Liquids—Having followed the passage of the gas through the plant, we shall now consider the flow of the liquids. The sulfuric acid formed in the last chamber (9) collects on the floor of the chamber, being the weakest (48° to 50° Bé., 59 to 62%) acid made in the system. It is also the purest, as explained below, and can be drawn off for separate concentration when a purer than ordinary chamber acid is required. Generally it flows into the next preceding chamber (7), where it is slightly strengthened by the stronger acid made in the warmer chamber. It is also slightly contaminated in (7), especially in a pyrites-burning plant, by the greater quantity of dust, As_2O_3, etc., in the fresher gas. It will also pick up a little more lead from the action of the warmer acid on the chamber walls. From there it passes to the first chamber (5), finally reaching 52° to 54° Bé. (65 to 68%). Thence it may be partly withdrawn for sale as "Chamber Acid" or taken to the storage tank (15).

Most or all of this acid is elevated from the tank to the top of the Glover tower (3) and run in along with the nitrous vitriol. At first it becomes stronger by admixture with the nitrous vitriol, then diluted by the upcoming steam. Meeting the SO_2 of the burner gases, the nitric acid and nitrosylsulfuric acid are decomposed and the resulting oxides of nitrogen are carried up by the burner-gases. As the acid trickles down, it is heated by the hot gases and thus becomes concentrated, flowing from the bottom of the tower into coolers (16) at a strength between 59° and 61° Bé. (76 to 79%). This is the "Glover-tower acid," salable as such. When pyrite is used, this acid contains most of the arsenic and dust not held back by the dust-catching devices (1). It generally contains a little SO_2 but is nearly free from oxides of nitrogen, though it is quite capable of dissolving them readily when cold.

A portion of this strong acid, after cooling, is elevated to the top of the final Gay-Lussac tower (14), where it trickles down against the flow of outgoing gases, thus dissolving and recovering the final portions of the nitrous gases. It is then sent to the preliminary Gay-Lussac (13), where it similarly meets the gases from the chamber and becomes "nitrous vitriol." From the bottom of the preliminary Gay-Lussac it flows to a storage tank (18), whence it is sent to the top of the Glover.

The quantity of acid pumped around the circuit of the Glover, final Gay-Lussac, preliminary Gay-Lussac, and back to Glover towers may be from one to four times the amount of acid produced by the plant. To enable better control of temperatures and densities, the pumps and piping are so arranged that part of the efflux of any tower may be returned to the top of the same tower, thus increasing the circulation on that tower. This is found particularly useful on the final Gay-Lussac tower.

CONSTRUCTION AND FUNCTION OF THE APPARATUS FOR CHAMBER PROCESS

Step No. 1: Preparation of the Sulfur Dioxide Gas—The making and cleaning of the sulfur-dioxide gas has been described earlier in this chapter. As there explained, it is customarily made richer than for the contact process (about 10% if made from brimstone) and need not be so thoroughly cleaned unless very pure acid is to be made. Inert dust, such as unburned sulfur, can be settled out in the chambers as sludge. Dust of metallic oxides merely forms soluble impurities in the finished acid.

Step No. 2: Making the "Niter-Gas"—The chamber process involves a continual loss of oxides of nitrogen, since the efficiency of their absorption in the Gay-Lussac towers is only about 85%. Formerly, the oxides of nitrogen were replenished by "potting niter" or by adding nitric acid, but commencing in 1926, the great majority of American chamber plants have turned to the oxidation of ammonia for this purpose.

In "niter-potting," sodium nitrate and 60° Bé. sulfuric acid are heated in cast-iron pots, forming nitric acid and other nitrous gases and (as by-product) "niter cake." The latter, a mixture of $NaHSO_4$ and Na_2SO_4, can sometimes be sold, but often is a waste product. The pots are sometimes (for economy) placed in the burner-gas flue; sometimes (for better control) separately fired.

The ammonia-oxidation process merely burns NH_3 gas catalytically by passing it, mixed with air, through a heated platinum gauze.[91] It gives a more uniform and easily controlled supply of a purer gas, avoids the trouble of disposing of niter cake, and in most localities is cheaper in operation.

Step No. 3: The Glover Tower—The functions of this tower are to cool the burner-gases, release the oxides of nitrogen from the nitrous vitriol, concentrate the chamber acid and generate steam. Incidentally, the SO_2 is partly oxidized and some H_2SO_4 is formed.

The burner-gas should enter the tower at 425° C. to 650° C. Higher temperatures damage the tower; lower temperatures decrease the efficiency of denitration of the nitrous vitriol and render difficult the concentration of Glover acid to 60° Bé. Careful thermal design of the incoming gas flues and the dust separators (and dust precipitators, if any) is relied upon to obtain the proper cooling. This involves calculating the proper balance between the insulation, the exposed surface, and the amount of gas to be cooled.

In operating the Glover tower, the inflow of chamber acid is regulated so that the acid discharged is 60° to 61° Bé., or a trifle lower in very cold weather. Sometimes water may have to be added to accomplish this. The inflow of nitrous vitriol is regulated to obtain the proper composition of the exit gas. This gas (SO_2, SO_3, N_2, O_2, NO, N_2O_3, N_2O_4, and steam) issues from the Glover tower at a temperature of 70° to 110° C. and is conducted through a lead flue to the blower or to the lead chambers.

Construction of Glover Tower. The modern Glover tower is essentially a tall, square, brick chamber (e.g., 10 to 15 feet square and 30 to 40 feet high), loosely filled for most of its height with packing or checker-work of brick or

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[91] See Chapter 8.

tile. The hot gases flow up, and the acids flow down, through the packing. All the masonry is of "acid-proof" brick, laid in "acid-proof" cement.

The walls are usually of uniform thickness (17 to 21 inches) from top to bottom. They are usually stayed together by external tie rods. Because of the great weight of packing, a foundation of reinforced concrete is generally used. This is raised about twelve feet off the ground to permit the acid to flow by gravity to the coolers. For protection of the concrete against spilled acid, an apron of 6-pound sheet lead (i.e., having a weight of 6 lbs. per sq. ft.) is spread over the foundation. A pan of 30- to 60-pound lead, with edges turned up 18 to 24 inches, is constructed over the apron. The pan is completely protected by a brick lining, the floor layer being three or more courses thick. The tower itself is built in the pan, its walls making a tight seal to the upturned edges thereof. A design formerly in common use made the pan extend a couple of feet out beyond the tower on all sides, forming a moat into which the acid flowed; this facilitated cleaning out sludge, but the fumes from the hot acid were a nuisance.

Inside the walls of the tower, heavy brick supports in the form of arches or pillars hold up the masonry grid on top of which the packing is laid; this leaves a space for the distribution of the gas. The packing is sometimes made up of special shapes carefully arranged (a hollow ring or hexagon with an internal helix is one favorite), sometimes of irregular pieces dumped in. It should be more loosely stacked in the lower part of the tower, because the hot gases require more cross-sectional area.

The roof of the tower is of 12-pound lead, hung from external steel supports. The packing stops about 4 feet below the roof, leaving a space for gas collection and for the installation of the acid-distributing pipes or sprays or splash-plates. These spread the acid uniformly, and are supplied from a mixing box which is connected with two tanks at the top of the tower; one tank contains chamber acid, the other Gay-Lussac acid (nitrous vitriol).

The gas-outlet flue, made of lead, is connected into the roof. The gas-inlet flue, made of masonry, enters the tower 18 or 20 inches from the floor at a steep downward pitch to minimize the effect of spattering acid. The acid outlet is an opening in the wall of the tower, level with the floor, through which the acid flows into a lead box lined with masonry and overflows through a Duriron pipe. A damming arrangement lifts the level of the acid sufficiently to seal the opening in the tower wall. The outlet conducts the hot acid to the acid coolers.

Usual design provides 200 to 350 cu. ft. of packed space per ton of sulfur per day. A rational evaluation of the required volume should be based on the strength of the gas as well as the amount of sulfur burned, and should take into account the wetted surface of the packing.[92]

Before 1914, when the Chemical Construction Co. introduced the all-masonry tower into this country,[93] Glover towers were completely sheathed in lead supported by a structural steel frame, and the walls were thinner toward the top. Other types of construction still sometimes used are: (1) circular or octagonal plan instead of square, (2) large quartz lumps as packing, gradu-

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[92] Zeisberg, Chem. and Met. Eng., *21*, 765 (1919).
[93] Fairlie, loc. cit., p. 169.

ating smaller toward the top, (3) cast-iron inlet flue instead of brick, (4) timber framework to support the lead sheathing. For detailed descriptions of this and other forms of Glover towers, see older editions of this Manual or consult the reading list at the end of this chapter.

Acid Coolers. The acid leaving the Glover tower will be 130° to 160° C.; it must be cooled for storage or for use in the Gay-Lussac towers, and to enable it to be handled in lead. The ordinary acid coolers are open vertical cylindrical lead tanks supported by a steel framework and filled with coils of lead pipe through which cold water circulates. Sometimes they have external water jackets to prevent corrosion of the tank-walls; if not, it is advisable to line at least the first cooler with "acid-proof" masonry. The acid-inlet pipe is of silicon-iron and dips below the surface of the acid in the cooler to avoid excessive fuming. At least three coolers, arranged in cascade for gravity flow, are usually employed.

Acid Pumps. Blow cases ("acid eggs") and air-lifts were formerly the only feasible method of elevating acid. They are now practically superseded by motor-driven centrifugal pumps. The latter may be of ordinary cast iron. high-silicon cast iron, bronze, hard lead, ceramic, glass or rubber-lined iron, according to the composition and temperature of the acid to be handled.

Step No. 4: Lead Chambers—*Classical Type.* The classical lead chamber is merely an enormous room, whose walls are of sheet lead exposed to outdoor air circulation but protected from rain by a roof. The walls and top are thin, usually weighing 6 pounds per square foot; the bottom, 10 to 15 pounds. The sheets are attached at short intervals to a steel framework. The chambers may be 20 to 30 feet wide, 20 to 30 feet high, and 50 to 150 feet long. A small plant may have three or four of these, a very large plant, twelve. They are placed at least 7 feet apart to permit air circulation, and are raised 10 or 12 feet off the ground to permit inspection and repair of the bottoms and provide gravity flow for the acid effluent. The volume of chamber-space provided was formerly 24 cubic feet per pound of sulfur burned per 24 hours; nowadays, by careful control and with at least ⅙ square foot of external surface per cubic foot, 7 cubic feet per pound is sufficient in ordinary weather and 6 cubic feet in winter.[94] This unit, cubic feet per pound of sulfur per day, is often designated "space rate," though actually it is the reciprocal of a rate. Greater output can be obtained by increasing the amount of niter in circulation, but the loss of niter in the exit stack will be greater unless the Gay-Lussac towers are increased in size.

Pure water is sprayed into the tops of chambers by means of atomizers. The walls are provided with thermometers and with devices for sampling the acid and measuring the depth of acid on the floor. Hydrometer readings are taken frequently and the water feed regulated accordingly. Sometimes each chamber has a sight glass for observing the color of the gases. The connecting flues may be located in various ways, except that inlet and outlet of a given chamber should be on different levels, e.g., left and right, bottom and top.

Inter-Chamber Towers—Many plants abroad have towers or columns of various sorts between the chambers to aid in cooling and mixing the gases. Their value in the long run is questionable. If packed, and fed with exter-

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[94] Fairlie, loc. cit., p. 189.

nally-cooled acid, they increase the output capacity of the chambers in proportion to the added cooling effect, but this effect can be more cheaply obtained in other ways. The added resistance to gas flow also increases power costs.

New Types of Chambers—Many modifications of the chamber have been developed, some with notable success. These are principally directed toward reducing the cost of the plant by providing better cooling and better mixing. Some dispense with void chambers and use only packed towers. The best-known of these chambers are the Mills-Packard, the Gaillard-Parrish, the Falding chamber, the Dior chamber, the Pratt process (obsolescent), the Wolskel plant and the Schmiedel-Klencke roller-boxes. Among tower processes may be mentioned the Anaconda packed-cell process, the Opl tower process, and the Petersen tower process. Operation of the reaction chambers and towers under high pressure has been proposed by Berl and others. Several of these systems will be described below; for descriptions of the others, consult the reading list at the end of this chapter.

FIG. 25. Mills-Packard Water-cooled Chambers.

Mills-Packard Water-Cooled Chambers—This system uses moderate-sized lead chambers cooled by water flowing down their external surfaces. The coefficient of heat transfer from walls to flowing water being much greater than from walls to air as in the conventional chambers, a much smaller wall surface suffices to carry away the heat of reaction due to a given acid-production rate, even in installations where the water is recirculated through a spray pond or cooling tower, and hence comes to the chambers not much cooler than the atmosphere.

A chamber-volume of 2.25 to 2.75 cubic feet per pound of sulfur burned per day is claimed to be sufficient in two of the plants operating in the United States; the chamber-volume thus is only about one-third as great as the best air-cooled chambers.

In order that the water may spread out to form a continuous sheet covering the entire walls, they are slightly sloped outward from top to bottom. The shape of the chambers is a frustrum of a cone, 40 to 50 feet high and 20 to

35 feet in diameter; the chambers more recently built are divided into halves by an alley, the walls of which also slope and are water-cooled. The slope of the walls in early designs was 1:8, i.e., one foot outward in 8 feet of height; this has been gradually reduced to 1:32. Early plants had horizontal gutters attached to the walls at vertical intervals of about 7 feet, to redistribute the water; these have been eliminated in later designs. The walls are supported at intervals by straps hung from a steel framework. No housing or building is required, as the sheet of water flowing over the lead walls is found to be sufficient protection against thermal disturbance by sun or rain. The total construction cost is said to be less than half that of conventional lead chambers of the same output; the ground occupied is also said to be less than half.

The metal temperatures of the lead walls are of course lower than in an air-cooled chamber, because of the higher coefficient of heat transfer on the outside of the walls. This promotes the thermo-circulation of the gas within the chamber and the formation of liquid acid on the walls. It should also reduce the rate of corrosion of the lead; tests have shown a loss of 6 to 10 ozs. per sq. ft. in 8 years' service of a lead wall weighing 7 lbs. per sq. ft.[95]

Gaillard-Parrish chambers, used abroad, are approximately cylindrical, 22 to 50 feet diameter by 45 to 70 feet high. In the top are placed one or more centrifugal "dispersers," each driven by a vertical motor whose shaft passes through the roof. These dash an umbrella-shaped shower of cool chamber acid against the walls all around, forming a curtain thereon to cool them and protect them from the gases. To keep this curtain spread out, the walls are usually made sloping inward from top to bottom. The splashings also form a fine mist which falls through the gases to the bottom. The acid is collected from the bottom, cooled to 40° C., diluted to 50° Bé., and carried back to the dispersers. Down-drafting seems to be best. Three chambers in series are the common set-up. The rating is 2.75 to 3.50 cu. ft. per pound of sulfur per day.

Schmiedel-Klencke "Roller-Boxes" have been effectively used in combination with regular chamber systems. They are long lead boxes each filled with three fluted rollers rotating at 250 to 600 r.p.m. The gases pass longitudinally through the boxes, and the rollers, dipping into the nitrous vitriol in the bottom of the box, throw it into the gas stream in the form of a spray. The complete Schmiedel-Klencke process, of which these boxes formed a part, comprised other novel features in apparatus and in process, but has not been entirely successful.[96]

The Anaconda Packed-Cell Process dispenses with chambers and uses packed towers instead, each divided into compartments by partitions. The volume of these totals about one cubic foot per pound of sulfur per day. Cooling is achieved by copious circulation of acid which is too dilute to absorb oxides of nitrogen. Addition of water maintains the acid at a proper dilution. The niter concentration used is about three times that usual in chamber plants.

Ernst Berl's High-Pressure Process was suggested by him as a result of an extensive research.[97, 98] The reactions here referred to are given earlier in

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[95] Fairlie, Chem. and Met. Eng., *44,* 728 (1937).
[96] Trans. Inst. Chem. Eng., (British) *5,* 34-41 (1927).
[97] Trans. Amer. Inst. Chem. Eng., *31,* 193 (1935).
[98] Chem. and Met. Eng., *41,* 571 (1934).

this chapter under the heading "Chemistry of the Chamber Process." Berl states that at atmospheric pressure, reaction (1), viz., $2NO + O_2 \rightarrow 2NO_2$, is much the slowest of the series, hence determines the overall velocity of the group of reactions. Being a trimolecular gas-phase reaction, its velocity is proportional to the cube of the pressure. At high pressures the effect of this reaction is nearly suppressed and reactions (4a) and (5a) govern the velocity. At a pressure of 13 atmospheres, he obtained a production rate equivalent to 3 tons of 60° Bé. acid per 24 hours per cubic meter of chamber space. This rate is equivalent to 0.022 cubic foot per pound of sulfur per day, viz., about 300 times the production per unit volume that is customarily obtained in lead chambers. The Gay-Lussac tower would also be much smaller than usual.

The assumption that the velocity of reaction (1) will be proportional to the cube of the pressure is of course valid only if the reverse reaction is negligible, i.e., at the commencement of the forward reaction. But since the NO_2 polymerizes instantly to N_2O_4, we can write the reaction as: $2NO + O_2 \rightleftarrows N_2O_4$, and near equilibrium the velocity would be approximately proportional to the square of the pressure. Berl finally concludes that the overall reaction rate is proportional to the square of the pressure, and by extrapolation to 33 atmospheres, deduces, even for a plant of large production, a chamber small enough to be feasibly constructed to withstand such pressures. Of course, the dissipation of the heat of reaction, and the difficulty of constructing the compressors and other pressure-tight equipment out of acid-proof materials, would constitute serious problems of design. Berl states that at 50 atmospheres the heat of reaction would be sufficient to concentrate the 60° Bé. acid to 66° Bé.

Step No. 5: The Gay-Lussac Tower—The construction and packing of the Gay-Lussac tower is essentially the same as that of the Glover tower. It may be built with walls of sheet lead, either bare or lined inside with "acid-proof" brick, or of masonry alone. The purpose of the brick lining in a lead tower is to take the lateral thrust of random packing. Self-supporting (stacked) packing needs no tower lining. If a tower is built of lead lined with brick, provision must be made for free circulation of acid between the lining and the brick, otherwise pockets of nitrous gases will become oxidized and corrode the lead.[99]

The cross-section may be round or octagonal, but is usually square. Approximately twice as much packed space is required in the Gay-Lussac as in the Glover. Since it is usually desirable not to have the Gay-Lussac taller than the Glover, there are ordinarily two or more of the former connected in series.

For efficient operation of the towers, the system should be kept cool; the gas should not be hotter than 60° C., the acid not hotter than 35° to 40° C.

Control of the Chamber Process—*Niter Control.* As might be expected, niter (i.e., mixed oxides of nitrogen) is the important variable. A temporary cessation of niter supply will cause a rapid fall of temperature in the first chamber, as much as 20° C. in a few hours, simultaneously reducing the strength of acid produced. The percentage of niter in the gases has a great influence on temperature, because, within wide limits, it controls the rate of pro-

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[99] Fairlie, "Sulfuric Acid Manufacture," p. 224.

duction of sulfuric acid without necessarily affecting the ultimate yield of acid or the consumption of niter. The simplest indication of niter conditions is the color of the gases. In the first half of the travel (cubical space) through the chambers, the niter is all in the reduced form (colorless NO). About the middle of the travel, if the process is working properly, a faint tint (yellowish N_2O_3) appears, and in the latter part of the last chamber a distinct red (N_2O_4).

.To prevent loss of "red gas" via the final vent-stack of the Gay-Lussac, it is necessary to adjust the supply of niter in the chambers so as to maintain a minute amount of SO_2 in the gas entering the front Gay-Lussac. An excess of niter also speeds up the reaction in the front chambers and increases unduly the strength of the chamber acid.

A deficiency of niter is even more objectionable than an excess. It is indicated by paleness of the last chamber, decreasing nitrous strength of Gay-Lussac acid, and possibly by red fumes in exit gases. The serious consequences of deficiency are: decrease of production, SO_2 escaping to the last chamber in too great quantity, with moisture, preventing proper formation of NO_2HOSO_2; reduction of niter to N_2O, not recoverable; passage of niter as NO with SO_2 to Gay-Lussac; decrease of absorption, which, added to decomposition of nitrous vitriol by SO_2, leads to loss of niter both in bottoms and at exit. Thus a deficiency rapidly becomes worse; in fact it is possible that within an hour or two the recovery of niter may completely cease and the plant have to be shut down with a loss of 3 to 6 hours' time.

The amount of niter in process is controlled by adjusting either the inflow of nitrous vitriol to the Glover tower or the rate of adding fresh niter to the front chamber.

The observation of the color of the gases, especially in the last chamber, is the traditional method of studying the operation of the chambers; but, unfortunately, by the time the colors have visibly changed, the system is already seriously out of balance. A method that more quickly indicates a departure from normal operation is to observe the temperature difference between two fixed locations in the travel of the gas through the chambers, e.g., the first chamber and the middle one. The more niter in the gas, the greater will be the temperature difference. A two-pen recording thermometer or pyrometer will draw a record of these temperatures on a chart, and can be arranged to control automatically the rate of supply of nitrous vitriol or of fresh niter gas.

A. M. Fairlie has developed[100, 101, 102] a method of control by means of systematic determinations of the SO_2 content of the gas at various parts of the plant. His criterion is the ratio between the SO_2 in the Glover entrance gas and that in one of the early chambers. He says, "The oxidation of sulfur dioxide, and consequently the diminution of the SO_2 percentage, proceeds the more rapidly, the greater the quantity of nitrogen-oxygen compounds present in the gas mixture, in proportion to the sulfur dioxide present, and conversely. To control the process efficiently, then, is to introduce at the front of the plant such a quantity of niter as will induce oxidation of the sulfur dioxide admitted

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[100] Fairlie, A. M., Trans. Amer. Inst. Chem. Eng., *9*, 319-332 (1916).
[101] Fairlie, "Sulfuric Acid Manufacture," pp. 272-280.
[102] U. S. Patents 1,205,723 and 1,205,724.

at that rate of speed found by experience to yield the highest recovery of niter in the niter-absorption apparatus."

Loss of Niter. A certain loss of niter is unavoidable, but inasmuch as it is an important item in the manufacturing cost of the acid, every effort is made to reduce its amount. Careful control of the process, a liberal circulation of acid over the towers and the avoidance of forcing the plant greatly beyond its normal capacity are the requisites. Niter is traditionally calculated as "$NaNO_3$, 96% pure," even though actually obtained by oxidation of ammonia. On this basis, the loss in brimstone plants usually amounts to between 2 and 4% of the weight of sulfur burned. In plants using pyrite or metallurgical gases it is 50% greater, because the weaker gas requires more niter in circulation per unit of sulfur.

Control of Water. The strength of the acid being made in the chambers is continually observed at drip-spouts. It is controlled by regulating the rate of admission of the water sprayed into the chambers. According to Ernst Berl,[103] the velocity of oxidation of SO_2 by nitrosylsulfuric acid (SO_5NH) in the presence of sulfuric acid, is greatest when the latter is 57.5% (46.7° Bé.); also "violet acid" (SO_5NH_2) decomposes fastest at 60 to 65% (48½° to 52° Bé.). Hence the value of keeping the acid formed in the chambers within this range. Moreover, if the acid became stronger than 68% (54° Bé.) it would hold out of the reaction zone considerable nitrosylsulfuric acid in solution. Such acid would be unsuitable for sale as "chamber acid"; it would also strongly corrode the lead pans. If the acid became too weak, the Glover tower would not be able to concentrate it sufficiently; there would also be a tendency to form nitric acid, which would corrode the lead.

CONCENTRATING SULFURIC ACID

Summary—As we have set forth earlier in this chapter, by far the cheapest method of strengthening the output of a chamber plant is by mixing it with contact acid, oleum, or even sulfur trioxide.[104] However, in industrial plants where large quantities of weak acid are formed as by-product and have to be concentrated for re-use, the addition of sufficient contact acid would produce a surplus amount. In these cases, concentrating by evaporation is necessary. The "sludge acid" from oil refineries is the principal instance of the use of this by-product. "Spent acid" from organic nitrations is also important.

In the construction of apparatus for concentrating sulfuric acid it must be noted that different strengths of acid have different corrosive properties, as set forth earlier in this chapter and explained in the appendix. At boiling temperatures, even when reduced by vacuum, lead is safe only up to 80% (61° Bé.). Steel and ordinary cast iron will withstand cold acid, in absence of strong agitation, if the acid is not weaker than 65 to 75% (52° to 58° Bé.), but, if the temperature reaches 50° C., the acid must be at least 93% (66° Bé.) to form the necessary protective coating of sulphate. Boiling acid above 80% (61° Bé.) is handled by the brittle high-silicon cast irons (14% Si) or by "Hastelloy D"

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[103] Berl, E., Chem. and Met. Eng., *41,* 571 (1934).
[104] Gilchrist, Refiner, *9* (*9*), 85 (1930).

(85% Ni, 10% Si, 3% Cu, 1.5% Al), though alloys of Fe-Si-Cr or Ni-Cr can be used, and of course platinum, gold, glass, quartz or ceramics.

It will be seen from Table 6 that the boiling points of the stronger sulfuric acids are very high, and that to reduce the boiling points to commercially feasible levels requires the use of high vacua or low partial pressures. Both systems are in commercial use. The high-vacuum processes use closed steam-heated vessels equipped with condensers. The partial-pressure systems work at atmospheric pressure and blow large quantities of heated air through or over the acid, thus simultaneously heating it and reducing the partial pressure of its vapor.

TABLE 6—BOILING POINTS OF SULFURIC ACID, DEG. C. AND COMPOSITION OF VAPOR

Per Cent H_2SO_4 by Weight			*Absolute Pressure, inches Hg:* *Vacuum, inches Hg:*							*Deg. Bé.*
In Liquid	*In Vapor*									
	Zeisberg	*Thomas and Barker*	*29.92* *0*	*3.92* *26*	*1.92* *28*	*0.92* *29*	*0.52* *29.4*	*0.32* *29.6*	*0.12* *29.8*	
30	....	....	108	57	43	28	20	16	−7	26.37
40	....	....	116	63	47	32	23	18	−3	34.06
50	....	....	126	72	56	41	31	23	4	41.38
60	....	....	141	87	71	56	46	38	18	48.48
70	....	....	164	110	93	77	67	59	39	55.23
75	1	....	181	126	109	92	82	73	53	58.40
80	2	....	201	143	126	108	98	89	68	61.30
85	4	1	225	164	146	127	116	107	85	63.72
90	16	8	256	194	174	156	143	133	111	65.30
93	37	25	276	213	193	174	161	151	128	65.96
95	55	48	302	232^c	211^c	191^c	176	164	143	[a]
96	66	61	312^c	241^c	220^c	199^c	184	173	152	[a]
97	78	76	324^c	251^c	229^c	208^c	193	182	161	[a]
98.3	98.3	98.3	338	264^c	242^c	220^c	205	194	172	[a]
99.23	....	100	313^b	244^b	223^b	202^b	187^b	175^b	153^b	[a]

[a] Above 66° the Baumé reading does not increase fast enough to be a useful indication of strength.

Table 6 also gives figures from two different sources on the composition of the vapor given off by sulfuric acids of various strengths. Acid of 98.3% H_2SO_4 is a constant-boiling mixture, giving off vapors of the same percentage composition as the liquid, hence this is the strongest acid that can be made by any evaporative method.

Notes on Table 6—The boiling points, except as noted, are abridged from data given by the National Lead Co.[105] and by Otto Mantius.[106] Those marked "b" were computed, and those for 90% and 93% were checked within a few degrees, by means of graphs of log p vs. $1/(T-30)$ which were plotted

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[105] Fairlie, "Sulfuric Acid Manufacture," p. 609.

[106] Otto Mantius, private communication.

from the work of Thomas and Barker[107] at 180° to 295° C. and of another experimenter at 25° to 70° C. The boiling points marked "c" were computed by similar plots correlating Mantius's figures with those listed under "b." Since Thomas and Barker's work was done by determining the weight of H_2SO_4 and of H_2O evaporated by air-streams, the plots of pressure are subject to uncertainty due to partial dissociation of the H_2SO_4 vapor.

The figures in the column headed "Zeisberg" were obtained from his published curve[108] for percentage composition of vapors at atmospheric pressure, assuming that the percentages are by weight. Those headed "Thomas and Barker"[107] were calculated from the weights of H_2SO_4 and H_2O found in their original experiments. This calculation does not involve partial pressures. (We have discarded two readings, apparently doubtful, at very low pressures.) Their work was done on acids of 89.2 to 99.2%, and at temperatures ranging down to 180° C. For the acids of 95 to 99%, no definite trend of vapor composition with respect to temperature is shown. For acids of 89.2% and 91.2%, the percentage of H_2SO_4 in the vapor at 180° to 190° C. is less than half what it is at 220° to 260° C. E. Mantius states[109] that at temperatures below 195° C. practically no H_2SO_4 is found in the vapor of acids below 95%.

Recovery of Oil-Refinery Sludge-Acid—Sludge-acid, separated from the oil-bearing refinery sludge by treatment with water and steam, contains hydrocarbons, naphthenes, phenols, tars, etc. Some varieties of oil require steam-treating in an autoclave at 50 to 150 lbs. pressure to remove as much of the hydrocarbons as possible by volatilization and charring. The open-tank treatment gives acid of 35 to 45% H_2SO_4, the autoclave 40 to 50%[110] or even up to 49° Bé.[111] If vacuum evaporation is to be used, the acid should then be allowed to stand in storage tanks to allow heavy impurities to settle out and foam to be skimmed off.

A strength corresponding to about 65° Bé., varying according to the character and quantity of the impurities and the temperature of the treatment, is the maximum to which heat-concentrating of these acids is commercially feasible. Beyond this, the reduction of H_2SO_4 to SO_2 by the hydrocarbons and suspended carbon becomes serious. Note that the Baumé gravity of these dirty acids is greater than pure acid of the same strength, on account of dissolved sodium sulfate and other salts and suspended carbon; 66° Bé. acid may contain 88 to 92% H_2SO_4, instead of the normal 93%.[112]

Vacuum Evaporation—*Simonson-Mantius.* Of the vacuum evaporators, the best-known is the Simonson-Mantius, made by the National Lead Co. It is made in two types, one for producing 80 to 83% acid (about 61° to 63° Bé.), the other for 93% (66° Bé.) to 97%. Both of these types consist essentially of a closed vertical cylindrical shell with internal steam-heating tubes. The shell is of steel lined with lead, inside of which is an acid-resisting masonry lining to protect the lead. Since the brick lining is a good heat insulator, the metal shell is kept cool by the outside atmosphere, and thus is less corroded

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[107] Thomas and Barker, J. Chem. Soc., *127* (*2*), 2820 ff. (1925).

[108] Zeisberg, F. C., Trans. Amer. Inst. Chem. Eng., *14*, 1-11 (1922).

[109] E. Mantius, private communication.

[110] "The Science of Petroleum," Oxford Univ. Press, 1938, pp. 2765, 2766.

[111] Fairlie, "Sulfuric Acid Manufacture," p. 293.

[112] "The Science of Petroleum," p. 2766.

by the acid. It also permits the metal to accumulate a protective coating of sulfate, which would otherwise be scrubbed away by the circulation of the boiling acid. For boiling acid stronger than 90%, it is even possible to omit the lead lining if two thicknesses of brick are used.

When using high vacuum, the condensing system consists of a large steam-jet vapor compressor, discharging into a counter-current barometric condenser. The air and incondensible gases are drawn out of this condenser by a two-stage steam ejector having the usual intercondenser between the stages. The water and condensed vapor from the barometric condenser pass away through a drop-pipe. This disposes of the evolved acid vapor, which would otherwise create a nuisance, but it is, of course, lost. The amount of acid thus lost is stated to be less than 1% of the product when concentrating to 93%, or less than 3% when concentrating to 97%.[113, 114] Theoretical calculations based on the vapor-composition figures of Thomas and Barker, from Table 6, give 0.7% and 2.7% loss for 93% and 97% respectively; based on the Zeisberg figures, these losses would be about 1.6% and 3.9%. However, on the assumption that the acid-richness of the vapor evolved by acid of a given strength is less at temperatures below 195° C., the losses at high vacuum may be considerably less than these figures.

The evaporators for the 80 to 83% product are made in sizes producing 5 to 70 tons per day. They are heated by coils of heavy-walled lead pipe, using steam at about 45 lbs. gage (145° C. steam temperature). For single units, batch-wise operation is used, as is customary with all high-concentration single-effect evaporators.

For larger installations, two or more units are used, operated continuously; each unit is divided into four compartments through which the acid flows in series. This arrangement, equally with batch-wise operation, ensures that the greater part of the evaporation is done from acids of comparatively low boiling points. With condenser water at ordinary temperatures (e.g., 25° C.), producing a vacuum of 28″, the boiling point of 80% acid is 126° C.; thus there is a temperature difference of 19° C. available for heat transmission through the coils, which should give a fair evaporating rate up to the end of the operation. As the acid strength increases and its boiling point consequently rises, the evaporating rate will of course fall off unless the vacuum or the steam pressure be increased. For instance, to boil 82% acid at the temperature assumed above (126° C.) would require a vacuum of 28.5″ and consequently cooling water 6° cooler than for 80% acid.

The evaporator for higher acid strengths (up to 97%) is illustrated in Fig. 26. These are made in sizes producing 10 to 120 tons per day, and are operated batch-wise. They are heated by closed-end tubes of silicon-iron, using steam at 150 lbs. gage (186° C.), or of "Hastelloy D" using steam at 300 lbs. gage (217° C.) or Dowtherm vapor at 20 lbs. gage (304° C.). Very high vacuum is needed to reduce the boiling point of these strong acids sufficiently below the steam temperature to obtain a reasonable rate of evaporation. For instance, 97% acid, at an absolute pressure of 0.2″ of mercury, boils at 172° C., giving only 14° temperature difference for 150-lb. steam. With 300-lb. steam,

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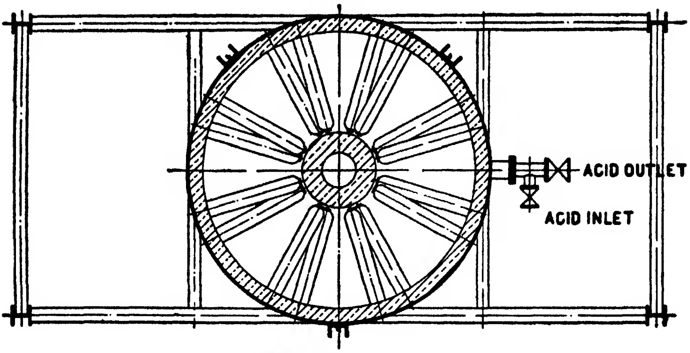
[113] Fairlie, "Sulfuric Acid Manufacture," p. 326.

[114] Otto Mantius, private communication.



SECTIONAL PLAN

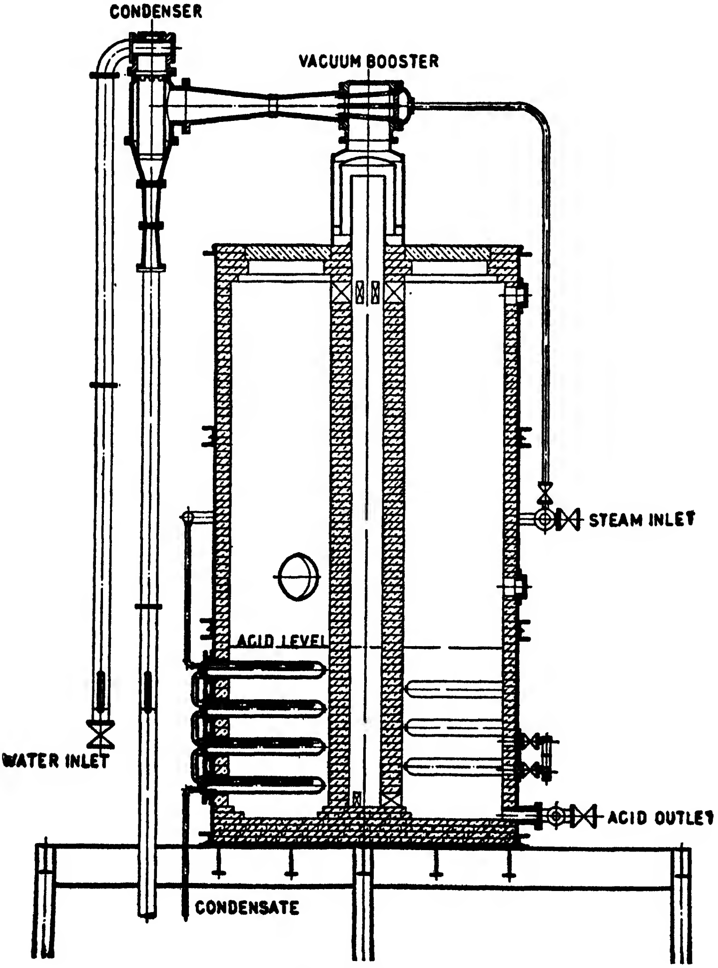


Fig. 26. Simonson-Mantius Vacuum Concentrator.

a lesser vacuum will suffice. Such a high vacuum necessitates the use of the steam-jet vapor compressor described above. Including the steam thus used, the total steam consumption per ton of acid produced, with 150-lb. steam pressure, is stated to be: [115]

	From 65% Acid	*From 78% Acid*
93.2% product	2250 pounds	1450 pounds
95% product	3000 "	2150 "
97% product	3670 "	2800 "

"Flash Film" Concentrator. The Calco Chemical Co. and the Chemical Construction Co. have a steam-heated concentrator especially useful in small sizes. It consists of a series of steam-jacketed pipes of acid-resisting iron. Steam at 400-lb. pressure (231° C.) can be used, as the type of construction is inherently strong, the steam pressure placing the alloy-iron in compression. Vacuum can be used or not, according to the strength of product desired and the steam pressure available. From the boiling-point chart it will be seen that the maximum strength of acid that can be satisfactorily boiled without vacuum by 400-lb. steam is about 83% (62.8° Bé.), which boils at 214° C.

Hot Gas Concentrators—*Drum Type.* The "Drum" concentrator, of the Chemical Construction Co., has recently been much in vogue. It is simple in construction; in its latest design, illustrated in Fig. 27, it consists essentially of a series of horizontal cylindrical steel tanks forming three compartments for acid and one used as an oil-fired furnace. The furnace is brick-lined, and into it the air for combustion is forced by a pressure blower. The three acid-compartments are lined with lead and with an acid-resisting masonry lining protecting the lead. The furnace gases, at about 590° C. (1100° F.), are bubbled through the acid in the front chamber; leaving it at about 235° C. (455° F.), they bubble through the middle chamber, through which is also bubbled a part of the hot furnace gas. The mixed gases leave this chamber at about 190° C. (375° F.) and are bubbled through the last chamber, from which they emerge at 120° to 150° C. (about 250° to 300° F.), carrying the evaporated vapor and some acid mist, also any volatile hydrocarbons not removed in the purification. They are then passed through a scrubbing tower or a Cottrell electrostatic precipitator to condense the vapor and catch the mist, unless the neighborhood is such that the nuisance of such escaping acid fume is permissible. A Cottrell is preferred to a water-fed tower, because the acid mist is recovered at full strength, usually 65 to 70%, instead of 30 to 40%. It is claimed that clean acid can be concentrated to 96% with only 1% loss.

The fresh acid is fed continuously into the rear chamber; it then flows through the others, counter-current to the gas. If dirty, before entering the front chamber it is sent to a skimming tank where carbonaceous matter is removed. The final concentration is done in the front chamber, where the hottest gas is available to finish the concentrating.

These concentrators are made in sizes to produce 15 to 125 tons per day. When producing 93% acid (66° Bé.), they are said to require 14 gallons of oil per ton of product if the feed is 50° Bé. (62.2%), or 35 gallons if the feed is 35° Bé. (41.3%).

[115] Otto Mantius, private communication.

Tower-and-Pan Type. Several modifications of the older type of concentrator are in wide use. They consist essentially of a covered acid-proof masonry pan connected at one end to a packed masonry preheating tower. Acid flows down this tower and fills the pan to the depth of about one foot. Combustion gases from an oil or gas furnace, at about 650° C. (1200° F.), are

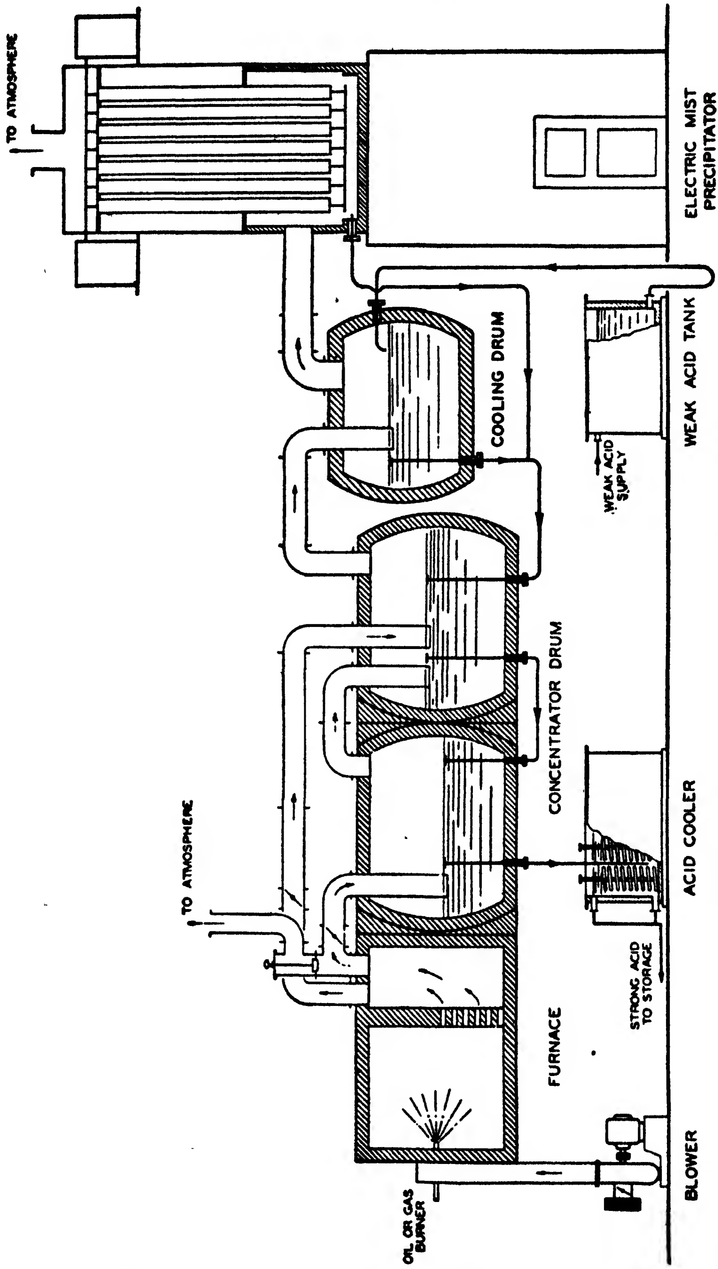


Fig. 27. The Drum-type Sulfuric Acid Concentrator.

drawn over the surface of the acid, or better, are bubbled through the acid, which is agitated by the flow of the hot gases or by bubbling a little compressed air through it. The acid is drawn off by overflow pipes at the end of the pan opposite the tower. The gases from the pan flow up the tower, heating and partly evaporating the fresh acid flowing down and giving up the strong acid fume carried from the pan. The gases leaving the tower, containing some acid mist, are then passed through a Cottrell electrostatic precipitator. These concentrators were built to produce acid as strong as 98% though the majority are operated to produce 93%.

Sludge-acid, unless very thoroughly purified, will foam when the concentration reaches 70% (55° Bé.). This is largely due to reduction of the acid to SO_2 by suspended carbon which begins to form, by decomposition, at about this strength. Adding dilute acid to hot acid of this strength will also cause foaming.[116] This foaming would give trouble in a tower-and-pan concentrator. It is therefore preferable to use two such concentrators, one producing acid of about 65% (52° Bé.) which is then cooled, settled, skimmed and sent to the tower of the second concentrator.

Other forms of concentrator working on the tower-and-pan principle, but different in construction, are the Kessler, the Gaillard, the Kalbperry, the Trepex, etc.[117] The Glover tower of a chamber plant also acts as a concentrator of this type.

Direct-Fired Concentrators—The oldest concentrators were pans or stills of various sorts heated by a fire or by the pyrites burner. If heated from an independent fire, they were usually arranged in a "cascade," consisting of a large number of basins arranged like a flat staircase of twenty or thirty steps. Each basin has a lip by which the acid overflows into the neighboring basin on the next step below. The acid is fed continuously at the top and the finished acid overflows from the last step. The lower portion of the cascade is hooded to carry off fumes. The furnace is under the lowest step, and the gases travel under the steps counter-current to the acid. According to the strength and purity of acid desired, the pans were of cast iron, lead, silicon-iron, porcelain, glass, "vitreosil" (fused quartz), platinum, or gold-lined platinum. The low coefficient of heat transfer from the hot gases to the pans demanded a large area of pans for even a modest output, thus requiring high initial cost. This, added to the incessant expense and nuisance of breakage or corrosion, has rendered these systems obsolete, except that cascade pans of vitreosil are still in use for small tonnages of very pure acid.

APPENDIX

A—HANDLING SULFURIC ACID

Corrosive Properties of Sulfuric Acid on Materials of Construction—Sulfuric acid with commercial impurities attacks practically all metals under one condition or another. The attack on lead is slow for cold acid less than

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[116] "The Science of Petroleum," p. 2767.

[117] Fairlie, "Sulfuric Acid Manufacture," pp. 316-320.

95%. At boiling temperatures, however, or even at the moderate temperatures used when boiling acid at high vacuum, lead is safe only up to concentrations of 80%. Steel and ordinary cast iron are vigorously attacked by dilute acid, but strong acid forms a coating of sulfate which protects the metal from further attack unless violent agitation of the acid washes away the coating. In practice, the attack of quiet acid on iron or steel, in the cold, is slow for acid exceeding 65% (52° Bé.), and commercially negligible above 75% (58° Bé.). Acid of 93% (66° Bé.) is commercially stored in steel tanks at temperatures up to 50° C. (122° F.), or, if perfectly quiet, 60° C. (140° F.). Oleum can be distilled in steel vessels.

Acid above 80% (61° Bé.) at high temperature was formerly handled in platinum, gold, glass, fused silica, "chemical" stoneware, or "acid-proof" brick, but in recent years a number of acid-resisting alloys have appeared on the market, some of which resist very well corrosion by hot and cold, and both strong and dilute, sulfuric acid. Notable among these are ferro-alloys of silicon and chromium, certain nickel-chromium or nickel-silicon alloys and (for acid up to 80%) a number of malleable bronze alloys, especially aluminum bronzes. The most resistant of these alloys are the high-silicon cast irons, known commercially as Corrosiron, Duriron, Tantiron, etc., containing 14 to 15% silicon; these are resistant to all concentrations of sulfuric acid at all temperatures.[118] They possess the disadvantages of being very brittle, not malleable, and can only be made as castings and can be machined only by grinding. "Hastelloy D" (85% Ni, 10% Si, 3% Cu, 1.5% Al) has similar properties but a much higher tensile strength. The usual "stainless steels" (containing 18% chromium and 8% nickel) are resistant to cold sulfuric acid of all concentrations, including oleum, if the acids contain dissolved air; but, if the acids are air-free or boiling, failure will occur. However, by greatly increasing the percentage of nickel, and in some cases the chromium, there have been obtained fairly hot-resistant alloys of quite good strength, malleability, and machineability. They are obtainable as castings and in certain rolled forms.

Monel metal[119] in the cold resists air-free sulfuric acid up to about 85% (64° Bé.); air-saturated acid between 50% and 85% is well resisted and below 50% almost as well; above 85% the attack increases rapidly. Temperature up to 105° C. does not increase the attack by air-free acid, but somewhat increases attack by air-bearing acid. Boiling acid above 75% (58° Bé.), since it has oxidizing properties of itself, seriously attacks Monel even in absence of air.

Tellurium lead (0.04 to 0.10% Te) is said to be much more resistant to sulfuric acid corrosion than pure "chemical" lead, and much stronger and tougher.[120] One large chamber, at least, has been built of it; this was in the South in 1934. Calcium is said to have an effect similar to tellurium. "Hard" lead, alloyed with antimony, while not as resistant as pure lead, is much stiffer; it is used for pumps, valves, etc. "Regulus metal" is lead alloyed with both antimony and tin; it has higher tensile strength than ordinary hard lead.

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[118] McKay, R. J., and Worthington, R., "Corrosion Resistance of Metals and Alloys," Reinhold Publishing Corp., New York, 1936, p. 275.

[119] McKay, loc. cit., p. 386; also International Nickel Co., "Bulletin T-3."

[120] McKay, loc. cit., p. 202; Fairlie, "Sulfuric Acid Manufacture," pp. 51-52.

Platinum is slightly attacked by boiling 93% acid, and more so by 98%; platinum pans used for evaporating such acids were often lined with gold.[121]

Gaseous acid, water vapor, SO_2, and small quantities of SO_3 do not affect either lead or iron, but condensation must be avoided or the strength of the condensate carefully considered. Liquid or dissolved SO_3, however, sometimes has a peculiar action on cast iron, appearing to enter the pores and disrupt the casting, sometimes with a violence approaching explosion. Steel, semi-steel and, to some extent malleable iron castings, may be used as substitutes in this case. Corrosion of genuine wrought-iron pipe by liquid acid is much less than that of steel, but it is to be remembered that the pipe ordinarily sold as wrought iron is really steel pipe.

The great hygroscopic action of sulfuric acid is an important factor in the corrosion of steel and iron vessels and pipes. If air is allowed free access, the acid rapidly dilutes itself by absorption of moisture from the air and corrosion proceeds quickly. Where iron and steel are used, therefore, air should either be dry or, as far as possible, excluded.

For further information about the corrosion resistance of special alloys consult the items in the "Reading List" at the end of this chapter.

Rubber-coated metal is useful for some purposes as it resists acid up to 50% (41° Bé.) and up to about 85° C. The coating is applied by rubber-manufacturing companies. As applied to a steel tank, it forms a one-piece lining protecting all joints, rivet-heads, etc. The impeller of a centrifugal fan can be similarly coated and the fan casing lined.

Asphalt mastic forms a satisfactory floor surface around tanks or wherever acid may be spilled. It is usually applied by means of heat as a coating one inch or thicker on a brick or concrete floor.

Silica (quartz or pure silica sand) is unattacked by sulfuric acid of any strength or temperature. Fused quartz (e.g., "Vitreosil") dishes can be used for evaporating the acid. Quartz finely ground and mixed with a little silicate of soda is used as a cement for laying up acid-proof brick in tower linings.

Sulfur is very resistant to cold acid, though slowly oxidized by concentrated boiling acid. It is often melted and poured into cavities difficult to fill by other acid-resisting materials.

Concrete is badly attacked by even dilute acid. So also are brickwork and masonry containing basic constituents such as alumina or lime.

Paints, varnishes, enamels, and lacquers are practically all attacked by strong acid, particularly when hot, though some will stand cold dilute acid.

Storage of Sulfuric Acid—Strong acid, 66° Bé. or 98%, and oleum are usually stored in steel tanks of large capacity, emptied preferably through a foot-valve in the bottom surrounded by a low upstand to prevent the drawing of mud. These tanks are usually flat-bottomed, cylindrical, with domed tops provided with a manhole and loose overhanging plate. As they are much too large to permit the application of air pressure for elevating the acid, it is customary to locate them on structural steel or concrete supports high enough to run the acid into cars by gravity. If this cannot be done, a battery of

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[121] Parrish and Snelling, "Sulphuric Acid Concentration," Vol. II, Ernest Benn, London, 1924, p. 55.

closed horizontal cylindrical tanks can be used, and the acid forced out by air pressure.

For storing acid of 58° Bé. (75%) or less, lead-lined storage vessels are preferable. These are generally wooden tanks strongly stayed and lined with 10-pound lead throughout. Very satisfactory storage vessels have been made by building reinforced concrete tanks, painting the interior of these tanks with pitch and lining the tank with lead. The foot-valve should be of the plug type, made of hard (antimonial) lead or porcelain. In the latter case, the seat of the valve is set by pouring in melted sulfur around it.

Storage tanks of moderate size (100 tons or less) are often permanently mounted on scales. Large tanks should have a float-operated indicator. It is undesirable to open the tanks in order to ascertain the amount of acid therein, because this tends to cause corrosion of the interior due to dilution of the acid by atmospheric moisture.

Shipping of Sulfuric Acid—Sulfuric acid is shipped in tank cars, tank wagons, drums or carboys, the choice of material being dictated by the strength of the acid. Ordinary steel can be used for acid of 75% (58° Bé.) or stronger. Weaker acids are not often shipped, as they require lead-lined tanks. Tank cars sometimes have a foot-valve or cock on the bottom of the tank for emptying, but the better practice is to force the acid out of the tank with compressed air and to have only a bolted flanged nipple on the bottom for cleaning. Steel drums are of the usual design, but with an asbestos or lead gasket under the screw-plug. They hold 500 to 1500 pounds of acid. The carboys in which small quantities of sulfuric acid are shipped hold about 180 pounds of acid, and consist of a glass bottle protected from breakage by a casing of some sort, generally a wooden box packed with hay, mineral wool, or asbestos.

B—KINETICS OF THE CONTACT REACTION

Rate of the Contact Reaction—It has been stated that this reaction is one of the most difficult problems in heterogeneous catalysis.[122] It includes, like all catalyses of gases by a solid, five steps:

1. Diffusion of reactants, through the adjacent gas layer, to the catalyst.
2. Adsorption of reactants on the catalyst surface.
3. The chemical change, which occurs at the catalyst surface.
4. Desorption of products of reaction from the catalyst surface.
5. Diffusion of products of reaction away from the catalyst.

Since these steps are consecutive the slowest one determines the rate of reaction.[123]

The relation of these separate steps to each other is obviously dependent on the physical structure of the catalyst as well as its chemical makeup. It is

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[122] Schwab, G. M., "Catalysis," tr. H. S. Taylor and R. Spence, D. Van Nostrand, New York, 1937, p. 278.

[123] Schwab, ibid., p. 219. Cf. Griffith, R. H., "Mechanism of Contact Catalysis," Oxford Univ. Press, 1936, p. ix of introduction; also Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press, 1933, 3rd Ed., p. 344; also Taylor, H. S., J. Amer. Chem. Soc., *53*, 578 (1931); also Maxted, "Catalysis and Its Industrial Applications," 1933, Chaps. 14 and 15.

not surprising, therefore, that the reaction-rate equations deduced by different investigators are not identical, or that the effect of temperature on reaction rate is different with different catalysts and different catalyst-carriers.

The rate of progress of steps (1), (2) and (3), at any temperature, varies approximately in proportion to the concentration of SO_2 existing at the instant, whereas steps (4) and (5) are slower the greater the concentration. The temperature coefficient (the increase in rate with increase of temperature) of steps (1) and (5) is small,[124] but of (2), (3) and (4) is very large. Thus, by a study of the effects of concentration and of temperature on the overall rate of reaction with any specific form of catalyst it is possible to gain some insight as to which of the five steps is with that catalyst the limiting one, and so form an idea as to how the chemical makeup or physical form of the catalyst mass, or the method of operation in practice, could be improved.

Mathematical Expressions of the Reaction Rate—Various mathematical equations to express the reaction velocity at constant temperature have been proposed by different investigators. Since the velocity gradually changes during the course of the reaction, decreasing as equilibrium is approached, it must of course be expressed as a differential equation which, when integrated between limits, gives the average velocity during the time defined by the limiting conditions. The best-known are Bodenstein and Fink's [125], Lewis and Ries's,[126] Taylor and Lenher's,[127] and Hung Y. Chang's.[128] These are all empirical, are based on experimental work done with platinum catalysts of various sorts, and of course assume the heat of the reaction to be removed as it progresses, so as to give strictly isothermal conditions. These equations are given in the paragraphs following.

A study of the first three of these equations was made some years ago by the junior author of this chapter, applying them to the experimental work of these three investigators and others. It was found that Taylor and Lenher's fitted the data best, therefore we use this in all our own calculations in this chapter.

Bodenstein and Fink.

$$\frac{dx}{dt} = k\frac{(SO_2)}{(SO_3)^{1/2}} \qquad \text{(Eq. 6)}$$

This states that the velocity at any instant is proportional to the concentration of SO_2 and inversely to the square root of the concentration of SO_3. This equation requires that the velocity shall not become zero until all the SO_2 has disappeared, i.e., that the equilibrium conversion is 100%; therefore it cannot truly represent the course of the reaction close to equilibrium. A second defect is that it takes no account of the effect of oxygen concentration in increasing the rate.

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[124] Hinshelwood, loc. cit., p. 339.

[125] Bodenstein, M., and Fink, C. G., Zeit. Phys. Chem., *60,* 12 (1907).

[126] Lewis, W. K., and Ries, E. D., Ind. and Eng. Chem., *19,* 835 (1927).

[127] Taylor, G. B., and Lenher, S., Zeit. Phys. Chem., Bodenstein Festband, p. 40 (1931).

[128] Chang, H. Y. (Thesis for D. Sc.), Abstracts of Sci. and Tech. Pub., Mass. Inst. of Tech., No. 6, July, 1930, pp. 49-53.

Lewis and Ries.

$$\frac{-dx}{dt} = b \cdot x \cdot \ln \frac{r_e}{r} \qquad \text{(Eq. 7)}$$

in which x = mols of SO_2 present per 100 mols of total gas originally present.
t = elapsed time.
r = ratio of SO_3 to SO_2 at any instant.
r_e = ratio of SO_3 to SO_2 at equilibrium.
b = "constant" of reaction-velocity; constant during the course of an isothermal reaction, but of course greater at higher temperatures.
ln = natural logarithm.

Note that the effect of oxygen concentration is implicit in r_e.

Hung Y. Chang.

$$-\frac{d[SO_2]}{d\theta} = k \frac{[SO_2]}{[SO_3]^{0.2}} \cdot \ln \frac{\rho_e}{\rho} \qquad \text{(Eq. 7a)}$$

Chang's θ, ρ_e, and ρ have the same meaning as Lewis's t, r_e and r. His $[SO_2]$ and $[SO_3]$ are partial pressures, in atmospheres. Thus his equation is a modification of Lewis's, with the addition of $[SO_3]^{0.2}$ in the denominator.

The temperature range of his work was 375° to 575° C. He found that the rate of the forward reaction did not increase continuously with temperature, but only up to a maximum, after which it decreased. He also states that the reaction rate increased with gas velocity, and more so at high temperatures. At 380° C., k varied as $V^{0.2}$, and at 580° C., as $V^{0.6}$. These two statements should be of value in converter design, but are not applicable to all forms of catalyst nor all rates of flow (cf. pages 320, 321 and 317).

Chang also gives an equation for the rate of the reverse reaction, i.e., the decomposition of SO_3 into SO_2 and O:

$$-\frac{d[SO_3]}{d\theta} = f[SO_3]^{0.2} \ln \frac{\rho}{\rho_e} \qquad \text{(Eq. 7b)}$$

The rate of this reaction increases continuously with temperature.

Taylor and Lenher.

$$\frac{-dx}{dt} = K_1 \frac{a - x}{(S + x)^{1/2}} \qquad \text{(Eq. 8)}^{129}$$

Taylor and Lenher made their experiments in a sealed vessel, i.e., at constant volume, and followed the course of the reaction by measuring the pressure change. Their nomenclature is:

x = pressure change at time t.
a = oxygen pressure at start of run minus oxygen pressure at equilibrium.
s = one-half of SO_3 pressure at start of run.

From the equation $2SO_2 + O_2 = 2SO_3$, it will be seen that the total pressure change is equal to the oxygen pressure change and equal to one-half of the SO_2 pressure change. Now let us introduce a nomenclature based on con-

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[129] There is a typographical error in the statement of the integrated form of this equation in the original article, line 26, p. 40; the exponent "½" has been omitted from the expression $(a + s)$ in the denominator of the first fraction.

stant pressure, and express the amounts of the gases as "mols per 100 mols of original unoxidized gas (real or hypothetical) containing no SO_3," thus:

X = mols SO_2 at the instant.
X_0 = mols SO_2 in original gas.
X_e = mols SO_2 at equilibrium.
Z = total mols of gas at the instant.
C = a factor to convert Taylor and Lenher's pressure units into "mols per 100 mols of original gas."

Then we can say:

$a = X_0 - X_e$.
$x = -(X - X_0)$.
s = zero.
$k = Ck_1$.

Then Taylor and Lenher's equation becomes:

$$-\frac{dx}{dt} = k\frac{(X - X_e)/Z}{\sqrt{(X_0 - X)/Z}}$$

$$-\frac{dx}{dt} = \left(\frac{k}{\sqrt{Z}}\right)\frac{X - X_e}{\sqrt{X_0 - X}} \qquad \text{(Eq. 9)}$$

In actual practice the term Z, which expresses the shrinkage in volume, can be neglected without introducing perceptible error. However, we shall retain it in our equations for the sake of completeness. Neglecting Z, Eq. 9 can be stated thus: "The rate of reaction at any instant is proportional to the volume of SO_2 that remains to be converted before equilibrium is reached (i.e., the 'distance to equilibrium') and inversely proportional to the volume of SO_3 existing." Thus this equation is practically derived from Bodenstein's by considering as an inert gas that SO_2 which will remain when equilibrium is reached.

In any experimental run in which the gas enters already partially converted ($SO_2 = X_1$) and leaves with an SO_2 content of X_2, by integrating Eq. 9, and substituting these limits, we obtain Eq. 10:

$$Kt = \sqrt{2kt} = \frac{1}{\sqrt{Z_m}}\left[2\sqrt{X_0 - X_1} - 2\sqrt{X_0 - X_2} + \sqrt{X_0 - X_e} \cdot \left(\ln\frac{\sqrt{X_0 - X_e} + \sqrt{X_0 - X_2}}{\sqrt{X_0 - X_e} - \sqrt{X_0 - X_2}} - \ln\frac{\sqrt{X_0 - X_e} + \sqrt{X_0 - X_1}}{\sqrt{X_0 - X_e} - \sqrt{X_0 - X_1}}\right)\right] \qquad \text{(Eq. 10)}$$

In this equation, "ln" signifies "natural logarithm," and Z_m = average total mols of gas during the reaction, i.e.:

$$Z_m = 100 - \frac{1}{4}\left(X_0 - \frac{X_1 + X_2}{2}\right) \qquad \text{(Eq. 10a)}$$

Equation 10 is really not as formidable as it looks. Except for the most critical work, one can neglect the influence of Z_m, i.e., assume $\sqrt{Z_m} = 10$. Besides correlating laboratory work, it is useful for approximate calculations on the partial conversions that a gas undergoes as it passes successively through the several parts of a commercial converter. The latter calculations are only approximate, because the reaction departs somewhat from isothermicity even in one tray or part of a converter.

For experiments that start with no SO_3 present, we have $X_1 = X_0$. Substituting in Equation 10, we obtain:

$$\mathrm{K}t = \frac{1}{\sqrt{Z_m}}\left[-2\sqrt{X_0 - X_2} + \sqrt{X_0 - X_e}\ \ln\left(\frac{\sqrt{X_0 - X_e} + \sqrt{X_0 - X_2}}{\sqrt{X_0 - X_e} - \sqrt{X_0 - X_2}}\right)\right] \qquad \text{(Eq. 11)}$$

Let A be the initial gas-strength $= X_0$

Let Q be the (fractional) conversion at any instant $= \dfrac{(X_0 - X_2)}{X_0}$

then $(X_0 - X_2) = QA$

Let Q_e be the (fractional) conversion at equilibrium $= \dfrac{X_0 - X_e}{X_0}$

then $(X_0 - X_e) = Q_eA$

Substituting this nomenclature, we obtain:

$$\mathrm{K}t = \frac{1}{\sqrt{Z_m}}\left[-2\sqrt{QA} + \sqrt{Q_eA}\ \ln\left(\frac{\sqrt{Q_eA} + \sqrt{QA}}{\sqrt{Q_eA} - \sqrt{QA}}\right)\right]$$

Simplifying, we obtain:

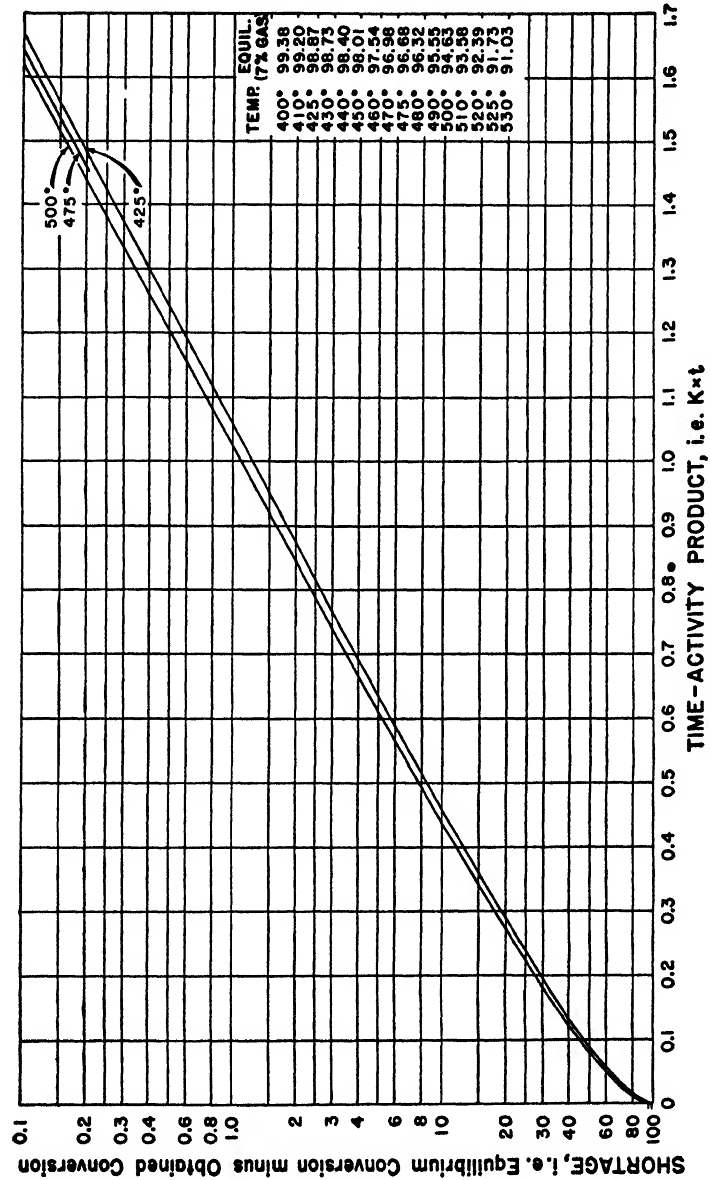
$$\mathrm{K}t = \frac{\sqrt{A}}{\sqrt{Z_m}}\left[\sqrt{Q_e}\ \ln\left(\frac{\sqrt{Q_e} + \sqrt{Q}}{\sqrt{Q_e} - \sqrt{Q}}\right) - 2\sqrt{Q}\right] \qquad \text{(Eq. 12)}$$

Computations of Expected Conversions—Equation 12 has several important uses. It enables the actual converting power of different catalysts to be evaluated quantitatively in terms of a standard. It predicts the effects of gas strength and of rate of gas flow in modifying conversions obtained.

As before, the value of $\sqrt{Z_m}$ can be taken as 10 for any but the most critical work. The meaning of t is not simply elapsed time, because in various parts of the reaction chamber and in the interstices of the catalyst there is always gas out of contact with the catalyst surface. Actually t is the time required for one volume of gas to pass over or through one volume of catalyst. "Volume of catalyst" is defined as the volume of a chamber into which the prepared catalyst ("contact mass") is poured or placed so as to fill it. If we measure the time in hours, t then becomes the reciprocal of the load-rate (usually denominated "space velocity") which is "volumes of gas per hour at 0° C. and 760 mm. per unit volume of catalyst."

Activity of a Catalyst—As will be seen from the preceding paragraph, the value of "K" directly measures the practical "activity" (i.e., commercial utility, or power) of the catalyst at the temperature in question. That is, if the "activity" of catalyst "A" is one-half as great as that of catalyst "B," then exactly two cubic feet of catalyst "A" will be required to do the same work as one cubic foot of catalyst "B." By "the same work" we mean the same percentage conversion of the same amount of gas of the same composition at the same temperature.

Assuming the strict applicability of Taylor and Lenher's differential equation (Eq. 8) to all catalysts (which is a rather bold assumption but appears to be approximately correct), a single test run theoretically suffices to determine the activity of a catalyst at the temperature of that run, provided of course that the conversion obtained is not too close to equilibrium.



TEMP.	EQUIL. (7% GAS)
400°	99.38
410°	99.20
425°	98.87
430°	98.73
440°	98.40
450°	98.01
460°	97.54
470°	96.98
475°	96.68
480°	96.32
490°	95.55
500°	94.63
510°	93.58
520°	92.39
525°	91.73
530°	91.03

FIG. 28. Time-activity Product During Progress of Contact Reaction. (Calculated for 7 per cent gas.)

To calculate, by Equation 12, the conversions to be expected for various ratios of gas flow to catalyst volume would necessitate a cut-and-try method. To facilitate such calculations, and also the calculation of activities from conversions observed, we have plotted Fig. 28. This gives values of K*t* computed by Equation 12, using the actual values of $\sqrt{Z_m}$. This graph is based on brimstone burner gas of 7% SO_2, and is only approximately applicable to other gas compositions. Comparison is possible only between runs of exactly the same temperature; these graphs give no indication of the effect of varying the temperature.

Use of the Graph to Evaluate Activities—In comparing the activities of two catalysts tested at the same flow rate, *t* is constant, and the abscissae are proportional to "K," the "activity."

Suppose we have tested two catalysts, "A" and "B," with 7% gas at 425°, all conditions and dimensions being the same, and we find that "A" gives 97.4% conversion and "B" gives 95.1%. From the table on the graph sheet we see that the equilibrium is 98.87. The "Shortage" for "A" is then $98.87 - 97.4 = 1.47$, which from the 425° graph we find equivalent to a "time-activity product" (K*t*) of 0.955. For "B" the shortage is $98.87 - 95.1 = 3.77$, and the activity is 0.709. The relative activity of "B" is thus 0.709/0.955 or 74% of the activity of "A."

Suppose now we have tested catalysts "C" and "D," passing gas at the same linear velocity through each, but "D" being disposed in a layer twice as deep as "C" and hence twice as great in quantity per unit of gas. Then *t* for catalyst "D" will be twice as great as for "C," and if, for instance, the graph gives $Kt = 0.60$ for the test on "C" and $Kt = 0.80$ for the test on "D," the activity of "D" is $0.80/2 \div 0.60$, or 67% of that of "C."

Effect of Linear Velocity on Conversion—If the linear velocity (i.e., the volume of gas per minute divided by the cross-section of the converter chamber) is not the same for the two tests to be compared, a true comparison of activities cannot be so definitely made. One would naturally expect high linear velocity to increase the reaction rate and hence the activity, because the increased turbulence would assist the diffusion of the reacting gases to and from the surface of the catalyst. However, in a current of gas flowing through the interstices between the pellets of a granular catalyst or between the fibres of an asbestos mat, the eddy currents are so complex and their variations with respect to velocity are so erratic that no quantitative relation between velocity and activity would be expected to be valid for all catalysts.

H. Y. Chang,[180] with a platinum catalyst, found K proportional to $V^{0.2}$ at 380° and to $V^{0.6}$ at 580°, *V* being the linear velocity. Tests in the present author's laboratory on two vanadium catalysts at high rates of flow have given much smaller exponents.

Use of the Graph to Compare Different Flow Rates with the Same Catalyst. In this case, since "activity" is constant, the abscissae are proportional to "time," or inversely to "flow rate," provided that the linear velocity is the same. Thus, suppose a certain catalyst tested with 7% gas at 450° gives 96.9% conversion at a flow of 75 cc. of gas per minute per 10 cc. of catalyst. What would it give with the same linear gas flow if the catalyst were only half as deep, i.e., 75 cc. of gas over 5 cc. of catalyst? The equilibrium is 98.01; the shortage is $98.01 - 96.9 = 1.11$; the "Time-Activity Product," interpolating between the 425° curve and the 475° curve, is 1.025. With 5 cc. of cata-

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[180] Loc. cit.

lyst, the time of contact is proportional to 5/10 of 1.025, or 0.513; whence the shortage is 7.9, and the conversion may be expected to be 98.01 − 7.9, or 90.1%.

Effect of Gas Strength on Conversion—We have already presented graphs giving the relation between gas strengths and equilibria. But commercial operations always do, and laboratory tests always should, stop short of equilibrium. In such cases, it is useful to be able to correlate results of tests made with gases of different strengths. For this purpose we present Tables 10 to 14, which we have computed by mechanical and graphical methods from Equation 12. These tables answer questions such as: "In a performance test with 9% gas at 425° C., a conversion of 93.4% was obtained. What would have been the conversion with 7% gas, other conditions being equal?" The answer is 95.0%. Note the following limitations in the use of these tables:

TABLES 7–11: EFFECT OF GAS STRENGTH ON ISOTHERMAL CONVERSION OF BRIMSTONE BURNER-GAS

TABLE 7—*400° C.*

6%	99.42	99.2	98.8	98.4	98.0	97.6	97.1	96.7	95.9	95.0	94.1	93.2	92.3
7%	99.38	99.0	98.5	98.0	97.5	97.0	96.5	96.0	95.0	94.0	93.0	92.0	91.0
8%	99.33	98.8	98.2	97.6	97.0	96.4	95.8	95.3	94.1	93.0	92.0	90.9	89.8
9%	99.28	98.6	97.8	97.1	96.5	95.8	95.2	94.6	93.3	92.1	90.9	89.8	88.7
10%	99.19	98.3	97.4	96.7	95.9	95.2	94.5	93.8	92.5	91.2	90.0	88.8	87.5

TABLE 8—*425° C.*

6%	98.94	98.3	97.5	96.7	95.8	95.0	94.1	93.2	91.3	86.6	81.8	77.0	72.1
7%	98.87	98.0	97.0	96.0	95.0	94.0	93.0	92.0	90.0	85.0	80.0	75.0	70.0
8%	98.78	97.6	96.5	95.3	94.2	93.1	92.0	90.9	88.7	83.5	78.3	73.2	68.2
9%	98.67	97.3	95.9	94.6	93.4	92.1	91.0	89.8	87.5	82.0	76.8	71.6	66.6
10%	98.53	96.8	95.3	93.9	92.5	91.2	90.0	88.7	86.3	80.7	75.3	70.1	65.0

TABLE 9—*450° C.*

6%	98.13	97.8	97.4	97.0	96.6	96.1	95.7	94.9	94.0	93.1	92.2	91.3	90.4
7%	98.01	97.5	97.0	96.5	96.0	95.5	95.0	94.0	93.0	92.0	91.0	90.0	89.0
8%	97.86	97.2	96.6	95.9	95.4	94.8	94.2	93.1	92.0	90.9	89.8	88.8	87.7
9%	97.67	96.8	96.1	95.3	94.7	94.1	93.4	92.2	91.0	89.8	88.7	87.5	86.4
10%	97.43	96.3	95.5	94.7	94.0	93.3	92.6	91.3	90.0	88.7	87.5	86.3	85.2

TABLE 10—*475° C.*

6%	96.87	96.7	96.4	96.0	95.6	95.2	94.8	93.9	93.0	92.2	91.2	90.3	89.4
7%	96.68	96.5	96.0	95.5	95.0	94.5	94.0	93.0	92.0	91.0	90.0	89.0	88.0
8%	96.44	96.2	95.5	94.9	94.3	93.8	93.2	92.1	91.0	89.9	88.8	87.7	86.6
9%	96.12	95.8	95.0	94.3	93.6	93.0	92.3	91.1	89.9	88.7	87.6	86.4	85.3
10%	95.72	95.3	94.3	93.6	92.8	92.1	91.4	90.1	88.8	87.5	86.3	85.1	84.0

TABLE 11—*500° C.*

6%	94.94	94.5	93.7	92.9	91.1	90.2	89.3	88.4	86.6	81.8	77.0	72.1	67.2
7%	94.63	94.0	93.0	92.0	90.0	89.0	88.0	87.0	85.0	80.0	75.0	70.0	65.0
8%	94.30	93.5	92.3	91.1	88.9	87.8	86.7	85.6	83.5	78.3	73.1	68.1	63.1
9%	93.83	92.8	91.4	90.1	87.7	86.5	85.4	84.3	82.0	76.6	71.4	66.3	61.3
10%	93.20	92.0	90.4	89.0	86.4	85.2	84.0	82.8	80.5	75.0	69.7	64.6	59.7

1. The conversion must be isothermal, i.e., the temperature must be held constant throughout the reaction.

2. The gas must be made by burning sulfur in air, or must have the same composition as gas so produced.

3. "Other conditions being equal" means the same volume of the same catalyst, the same volume of gas per hour, the same dimensions of container (to assure the same linear gas velocity) and the same temperature.

4. The tables are completely independent of each other; they give no comparison between different temperatures.

In each table, the five values in any one column are conversions equivalent to each other in catalytic power. For example, if a certain volume of catalyst at 400° C. acting on a certain volume per hour of 6% gas effects a conversion of 98.0%, the same volume of 7% gas would have been converted 97.5%, and the same volume of 8% gas would have been converted 97.0%.

The first column of conversions are the equilibrium conversions.

SO_2-Air Mixtures vs. Burner-Gas—It is well known that, under identical conditions, any mixture of SO_2 and air will always give a higher percentage conversion to SO_3 than will a gas of identical SO_2 content made by burning brimstone (sulfur) in air. This is due to the greater oxygen content of the SO_2-air mixture, which raises the equilibrium and slightly increases the velocity of reaction.

In Tables 12 and 13, a set of figures has been prepared whereby, from the experimental results obtained isothermally with SO_2-air mixtures, one can calculate what the conversion would have been if burner-gas of the same SO_2 content had been passed at the same rate over the same amount of the same catalyst at the same temperature. Table 12 is merely a statement of the difference in equilibria between SO_2-air mixtures and brimstone-burner gas. Table 13 was constructed by calculations based on Equation 12, via Figure 28. Its meaning and use will be clear from the following example.

TABLE 12—EXCESS OF EQUILIBRIUM CONVERSION OF SO_2-AIR MIXTURES OVER BRIMSTONE-BURNER GASES OF SAME SO_2 CONTENT

SO_2.....	*6.0%*	*6.5%*	*7.0%*	*7.5%*	*8.0%*	*8.5%*	*9.0%*	*9.5%*	*10.0%*
400° C...	.09	.10	.12	.14	.16	.18	.20	.23	.28
425° C...	.15	.18	.21	.24	.28	.33	.37	.43	.49
450° C...	.28	.32	.37	.43	.49	.56	.64	.74	.84
475° C...	.46	.53	.60	.68	.79	.91	1.05	1.21	1.39
500° C...	.75	.86	.98	1.10	1.23	1.39	1.62	1.88	2.16

TABLE 13—FRACTION OF COMPLETION OF TABLE 12, FOR VARIOUS CONVERSIONS OBTAINED WITH SO_2-AIR MIXTURES.

Conv.....	*98*	*97*	*96*	*95*	*94*	*93*	*92*	*91*	*90*	*88*	*85*	*80*	*75*	*70*	*65*
400° C...	.96	.94	.92	.90	.88	.86	.85	.84	.82	.80	.76	.69	.64	.58	.53
425° C...	.97	.95	.92	.91	.89	.87	.85	.84	.82	.80	.76	.69	.64	.58	.53
450° C...	.98	.96	.93	.91	.90	.88	.86	.85	.83	.80	.77	.69	.64	.58	.53
475° C...	*	.99	.96	.94	.92	.90	.88	.86	.85	.82	.78	.71	.65	.59	.54
500° C...	*	*	*	.98	.96	.93	.91	.89	.88	.84	.80	.73	.66	.60	.55

* Greater than equilibrium, hence impossible.

Suppose we have made a performance test at 475° with a mixture of 8% SO_2 and 92% air, and obtained 93.0% conversion. In Table 12 under 8.0% and opposite 475° we find 0.79. In Table 13 under 93% and opposite 475° we find 0.90. Multiplying 0.79 by 0.90 we obtain 0.71; this we subtract from 93.0 and conclude that 92.29% conversion would have been obtained (instead

TABLE 14—TEMPERATURE COEFFICIENT (PER 10° C.) OF THE REACTION RATE

Range, ° C.	*155° -248°*	*400° -425°*	*425° -450°*	*450° -475°*	*475° -500°*	*500° -525°*	*525° -547°*	*525° -565°*	*665° -700°*	*Authority*
Platinum	1.35–1.40	....	....	....	....	....	....	....	....	Bodenstein [131]
Platinum	....	....	....	....	....	....	....	1.12	1.09	Taylor [132]
Platinum	....	1.29†	1.13‡	....	....	....	....	....	....	* Lewis [133]
Tin Vanadate	....	1.3	1.9	1.49	1.34	1.25	1.20	....	....	* Maxted [134]
Vanadium (Calco)	....	2.22	1.88	1.28	1.19	1.18	....	....	....	Grosvenor [135]
Vanadium (Selden)	....	2.15	1.34	1.22	1.1	....	....	....	....	"
§ Vanadium on pumice 110 microns	....	....	....	1.68	1.67	....	....	....	....	Grosvenor[135]
" " " 72 "	....	....	....	1.67	1.53	....	....	....	....	"
" " " 41 "	....	....	....	1.52	1.41	....	....	....	....	"
" " " 30 "	....	....	....	1.92	1.50	....	....	....	....	"
" " " 21 "	....	....	....	1.82	1.38	....	....	....	....	"
" " " 11 "	....	....	....	1.85	1.06	....	....	....	....	"
" " " 1.5 "	....	....	....	1.48	1.04	....	....	....	....	"

* Calculated by the present authors from the published data.
† Actually the range was 400° to 420°.
‡ 420° to 435° and 435° to 450° both gave 1.13.
§ Experimental catalysts, Slama-Wolf patent, on sized pumice of the particle sizes given.

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[131] Bodenstein and Fink, Z. Phys. Chem. *60,* 40, Table 29.

[132] Taylor and Lenher, Z. Phys. Chem., Bodenstein Festband 1931, p. 42.

[133] Lewis and Ries, Ind. and Eng. Chem., *19,* 831.

[134] Maxted, E. B., and Hassid, N. J., J. Soc. Chem. Ind., Oct. 23, 1931, p. 400 T.

[135] W. M. Grosvenor et al., unpublished work

of 93.0%) if the gas had been brimstone-burner gas containing 8% SO_2 (instead of SO_2-air mixture containing 8% SO_2).

Temperature Coefficient of the Reaction Rate—Since, as already stated, the effect of temperature is not the same on each of the five steps comprising the catalysis, and the relative importance of those steps varies with temperature and with the makeup of the catalyst, the overall temperature coefficient of the reaction rate (i.e., of the activity of the catalyst, defined as "K" in Equation 12) varies in the same manner. One useful approximation, stated by Jaeger[186] and widely quoted, is that the reaction rate at 500° C. is forty times as great as at 400°; this is equivalent to an average temperature coefficient of 1.45 per 10° over this range. In general, vanadium catalysts have a greater temperature coefficient than platinum catalysts; at temperatures below 450° their activity falls off rapidly. Typical values for various catalysts are shown in Table 14; the values given are of course not strictly comparable unless calculated by the same reaction-rate equation.

Some authorities have stated that the reaction rate reaches a maximum at 500° to 550°, but Taylor's work quoted in Table 14 shows positive temperature coefficients even up to 700°.

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CHAPTER 8

THE NITROGEN COMPOUNDS

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Nitrogen compounds are becoming increasingly important in our industrial life, both in war and in peace. They are the common denominator of nearly all military and commercial explosives.[1] They form one of the three most essential groups of compounds necessary for fertilization of plants.[2] Without a limitless supply of such fertilizing material, the population of the world would undoubtedly be faced with eventual starvation. They are the basis of a large group of synthetic plastics and fibers.[3] They are the backbone of a large part of the dye industry.[4] Miscellaneous useful products of nitrogen compounds number into the hundreds.

Until the last few decades the only available large sources of supply of nitrogenous compounds for industrial use were by products from the distillation of coal [5] and the limited deposits of Chile saltpeter.[6] These sources are definitely limited in extent so other sources of nitrogen compounds are absolutely essential for permanent chemical industry. Hence, the development of methods of fixing the elemental nitrogen of the air into usable compounds is one of the most significant as well as one of the most interesting aspects of modern chemical industry.

FIXATION OF NITROGEN

W. S. Landis

The enormous development of industry based upon the fixation of atmospheric nitrogen into useful chemical compounds, is thought by many to have started after the outbreak of the World War in 1914. It is true that by 1915 Germany and Austria were forced to look elsewhere for their supply of nitric acid, for importation of Chilean nitrate was impossible. The industry, however, while receiving a tremendous impetus during the war period and thereafter, was nevertheless on a well developed commercial basis long previously. At least two of the processes which reached an important state of productive capac-

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[1] See Chapter 32.
[2] See Chapter 13.
[3] See Chapter 31.
[4] See Chapter 28.
[5] See Chapter 15.
[6] See Chapter 9.

ity, were highly developed at the outbreak of the war and the third process was operating at least in pilot plant stage. The war, therefore, merely forced intensive construction programs based upon already well-proven processes.

Arc Process—It had been known for over one hundred years that the passage of a current of air through an electric arc brought about a combination of the nitrogen and oxygen in the air to form an oxide of nitrogen. This oxide of nitrogen, by purely chemical operations, can be transformed into nitric acid or a corresponding nitrate. Prior to the war, plants using this principle had sprung up in various parts of the world each with its own type of arc furnace, but all using essentially the same process for converting the products of the furnace into nitric acid and nitrates.

In the arc process, air, sometimes preheated, was passed through an electric arc. The temperature was thus raised to about 3000° C. and the nitrogen and oxygen combined directly to form nitric oxide.

In an operating plant the gases leaving the arc carry from 1 to 2 per cent of NO after cooling. The subsequent treatment of these gases involves first, a very rapid chilling down to 1200° C. Then the temperature must be further reduced down to substantially normal conditions, but the speed of this cooling is not so important as in the first stages. The cooled gases are sent to scrubbing towers[7] operated in counter-current system with a feed of fresh water into the last tower. A nitric acid of 35 per cent strength is produced which can then be concentrated or converted into one of the several nitrate salts in separate operation. To insure complete recovery of the nitric oxides, additional towers fed with caustic soda or soda ash solutions recover sodium nitrate and sodium nitrite, which can be separated by crystallization.

The largest development was in Norway, where at one time 400,000 H.P. of electrical energy was used to produce nitric acid.

At one time there was more than 600,000 H.P. of electric energy used in the arc process plants for the fixation of nitrogen. Energy requirements of the more highly developed units are 12 horsepower years per short ton of fixed nitrogen in the form of nitric acid.

Attention should be called to the fact that, while the larger and more important installations of the arc process occurred in Europe, the first attempt to commercialize a process based upon this principle of operation was made at Niagara Falls, New York, by Bradley and Lovejoy in 1902-3. They used a large number of very small arcs in their furnace rather than one large arc of the type so successfully developed in several directions by the Europeans. The electrical equipment needed to control the currents in these small arcs was quite complex and relatively expensive, not to mention that it was subject to very easy derangement in its then early development. In consequence of the large amount of investment required and of the troublesome problem of up-keep this first commercial attempt at Niagara Falls was not a financial success, and subsequent development passed to Europe.

The process itself is now obsolete except for a small production in several scattered parts of the world, but the principles developed are still made use of in other directions. For example, if a mixture of nitrogen and hydro-carbon gas, or preferably ammonia and hydro-carbon gas, is passed through an arc similar to

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[7] See Chapter 2 for details of scrubbing towers.

those formerly used in the fixation of atmospheric nitrogen, hydrocyanic acid will be produced which can be recovered by suitable scrubbing and fractionating equipment. There are at least two such installations operating at the present time. It is not unlikely that other applications of this arc principle for the treatment of gases may once more bring this type of high temperature reaction furnace into operation.

FIG. 1. Cyanamid Ovens. (Courtesy North American Cyanamid, Limited)

Cyanamid—Nitrogen is absorbed by hot calcium carbide, forming what is known in the trade as Cyanamid. The reaction involved in the absorption is a reversible one, as follows:

$$CaC_2 + N_2 \rightleftarrows CaCN_2 + C$$

The first commercial plant was established in Germany in 1903-4 but in 1905 a very greatly improved plant was developed in Italy and since that date the process has been scattered widely in many parts of the world and there are now about thirty-five plants in operation with a capacity of about 450,000 tons of nitrogen contained in 2,000,000 tons of product.

Calcium carbide is first made from lime and carbon by the usual electric furnace process.[8] This carbide is then finely ground and the powdered material is charged into a special form of electric furnace where it is kept at 1000° C. See Figure 1. Pure dry nitrogen, produced by the copper or the Linde process, is then passed over the hot carbide and is there absorbed. Starting with a carbide containing 75 to 80 per cent calcium carbide, from 80 to 90 per cent of the theoretical amount of nitrogen will be absorbed, the resulting product being a grayish-black mass of calcium cyanamide, carbon, and lime. It contains on the

[8] See Chapter 12.

average 24 per cent nitrogen. The process requires about 1½ H.P. years per ton of nitrogen fixed.

The American fertilizer manufacturers require that the material be freed from undecomposed carbide and caustic lime before they can use it. The product is therefore hydrated in specially designed rotary mixing apparatus before appearing upon the market. A small quantity of mineral oil is added to assist in keeping down the dust. This hydrated, oiled material is sold in the United States under the trade name Cyanamid.

If Cyanamid is treated with superheated steam its nitrogen content is quantitatively evolved as ammonia, according to the reaction:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

One large installation for the conversion of Cyanamid into ammonia is in operation in the United States, the ammonia being transformed into various salts.

When treated with warm water dicyandiamid is formed:

$$2CaCN_2 + 4H_2O = 2Ca(OH)_2 + (CNNH_2)_2$$

A solution of calcium cyanamide when treated with excess of mineral acid forms urea,[9] which can be recovered in highly purified form by evaporation and crystallization.

When fused with common salt, sodium cyanide is formed. All of these derivatives are becoming of greater importance as a consumer of Cyanamid each year.

AMMONIA SYNTHESIS

The synthesis of ammonia from its elements, nitrogen and hydrogen, has been a commercial accomplishment since 1913, when the Badische Anilin & Soda Fabrik placed their first small commercial unit in regular operation. The reaction is:

$$N_2 + 3H_2 = 2NH_3 + 21{,}880 \text{ cal. at } 20° \text{ C}$$

Today there are a large number of modifications of the original process installed throughout the world differing more or less in the sources of raw materials and in the preparation of hydrogen, but more or less alike in the general principle of directly combining the nitrogen and hydrogen to form ammonia. By far the larger proportion of atmospheric nitrogen fixed today throughout the world is from the synthetic ammonia process.

The basic principles utilized in combining nitrogen and hydrogen were developed by Haber in Germany. He found that by taking a mixture of carefully purified nitrogen and hydrogen in the volume proportion of 1 to 3, compressing this mixture to 200 atmospheres or above, and then passing it over a heated catalyst at temperatures of low redness, a considerable proportion of the nitrogen and hydrogen would combine to form ammonia. This could be washed out of the exit gases and recovered in the form of ammonia solution, and the unreacted gases returned to the apparatus. Later Bosch developed a process of producing the mixture of purified gases in large quantity and by combination of the two processes, one the preparation of raw materials and the other the synthesis, the

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[9] See also Compound 23, Chapter 27.

operation became commercial. In consequence the original German process frequently goes under the name of Haber-Bosch synthetic ammonia process.

Preparation of Materials—The Synthetic Ammonia Process may well be divided into two entirely distinct operations. The first is the preparation of the mixture of hydrogen and nitrogen. The second operation is the synthesis of the ammonia from this gas mixture.

For the preparation of nitrogen we have several available processes. The liquefaction of air and the separation into its constituents, nitrogen and oxygen, is an old and highly developed art. Single units with a capacity up to 150,000 cu. ft. of nitrogen per hour are available from a number of manufacturers. Other systems of producing nitrogen satisfactory for this gas mixture can be incorporated as a part of the hydrogen producing process, such as burning oxygen from air by hydrogen, followed by condensation of the water.

For the production of hydrogen, the Bosch system is most widely used. In this system coke is burned in a water-gas producer to produce blue water gas $CO + H_2$. For ammonia production there is nothing new or novel in either the producer or its operation, this being a highly developed art in the illuminating gas industry. The blue gas may be mixed with a certain quantity of producer gas,[10] the quantity of producer gas added being such that the nitrogen introduced in the producer gas will bear the right ratio to the hydrogen of the ultimate gas mixture.

This mixture of blue gas and producer gas containing nitrogen and hydrogen, carbon monoxide and carbon dioxide, is freed from all dust and tar. It is then mixed with a large excess of steam and the mixture heated in a counter-current exchanger. The hot steam-gas mixture is then passed through a catalyst made up of a mixture of oxides of iron and chromium in which the iron predominates to promote the so-called "shift" reaction. A small portion of the steam present oxidizes the carbon monoxide to carbon dioxide and returns hydrogen to the mixture by the reactions

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

After leaving through the counter-current heater, this gas mixture, now containing nitrogen, hydrogen, carbon dioxide and only a small proportion of carbon monoxide, but carrying with it a large excess of steam, is passed through condensers which eliminate the steam. It is next compressed to about 20 atmospheres and under this pressure is sent to scrubbing towers where the carbon dioxide is washed out with water. The resulting gas, containing nitrogen and hydrogen and a very small percentage of carbon monoxide, again returns to the compressors for compression to 200 atmospheres or more, and under this high pressure is washed with an ammonium cuprous formate solution which takes out all of the impurities, leaving only the highly purified mixture of nitrogen and hydrogen.

Figure 2 is a photograph of a gas producer operating in a European synthetic ammonia plant for the production of blue gas.

Other Sources of Nitrogen and Hydrogen—In the process described above, coke and steam were the source of the hydrogen, and coke of the nitrogen. In some cases, the process has been modified so that the nitrogen, instead of coming from producer gas, is derived from liquid air equipment.

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[10] See Chapter 19.

Still other sources of hydrogen are available. By the electrolysis of water[11] hydrogen of high degree of purity can be produced. This hydrogen is mixed with nitrogen from the liquid air plant. In such a process coal or coke is not needed and all the energy can be supplied as electricity, either for the electrochemical action in the hydrogen cells, or for the motors used to drive the pumps, compressors, etc. This process is particularly favorable for use in regions where there is hydroelectric power, but little coal.

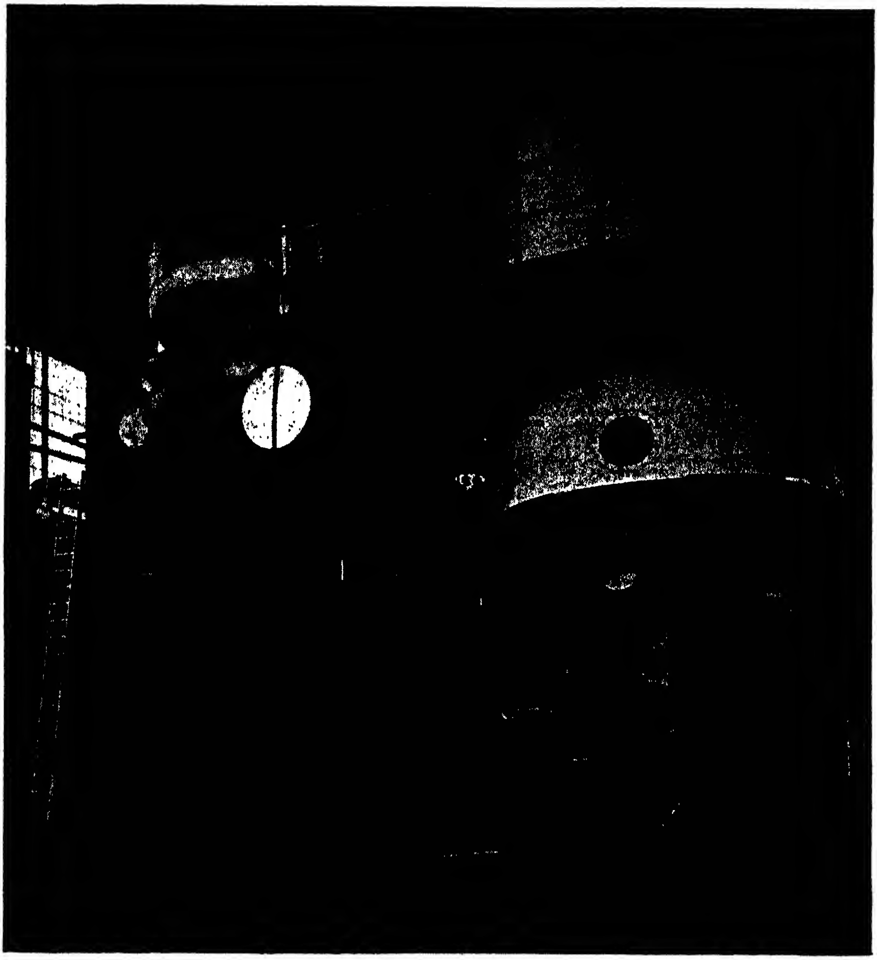

FIG. 2. Producer for Making Blue Water Gas.

The apparatus used for the production of electrolytic hydrogen or of blue gas and producer gas is standard for many other industries.

Hydrogen can also be produced from coke-oven gas. Gases from the by-product coke ovens contain 40 to 50 per cent of hydrogen. This gas can be compressed and liquefied and the hydrogen separated by distillation and rectification.

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[11] See Chapter 12.

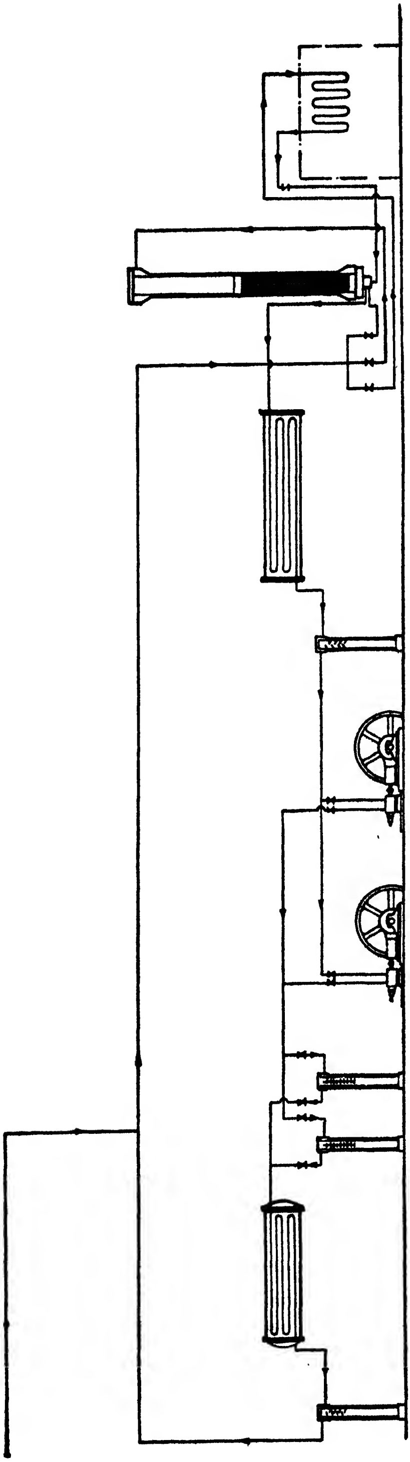

FIG. 3. Flow-sheet of Ammonia Synthesis Apparatus.

This is a common source of hydrogen in Europe in many synthetic ammonia plants. It is customary to liquefy the coke-oven gas by cooling with liquid air and washing the hydrogen with liquid nitrogen to insure freedom of all harmful impurities. This involves two to three sets of liquefaction apparatus, when one includes the production of nitrogen for the ultimate gas mixture.

To increase the hydrogen yield the coke oven gas may be cracked, either with or without steam admixture, and the cracked gas treated as described above in the Bosch method of handling blue water gas.

THE HABER PROCESS

The purified mixture containing one volume of nitrogen to three volumes of hydrogen next goes to the ammonia synthesis apparatus. In the apparatus the gases are preheated by counter-current exchange and then through a catalyst bed consisting essentially of granulated oxides of iron combined with alkali, alkali earth, and other promoters. Here, portions of the gases combine to form ammonia, the proportion depending upon the system used and the pressure to which the gas has been subjected. In the Haber-Bosch process operating at 200 atmospheres, about 8 per cent of the gases sent through the catalyzer combine to form ammonia. Under the higher pressures used in other systems, as much as 20 per cent may be combined in such a single pass through the catalyzer.[12]

[12] For the presentation of more details and a discussion of the principles of high pressure synthesis, see Chapter 4.

After leaving the catalyzer, the gases are either refrigerated or scrubbed to remove ammonia and returned to the catalyzer apparatus by the aid of a small circulating compressor. Fresh gas mixture is fed to the system to replace that converted into ammonia. A pictorial flow-sheet of the compressed mixture of gases through the ammonia synthesis apparatus is shown in Figure 3. This is

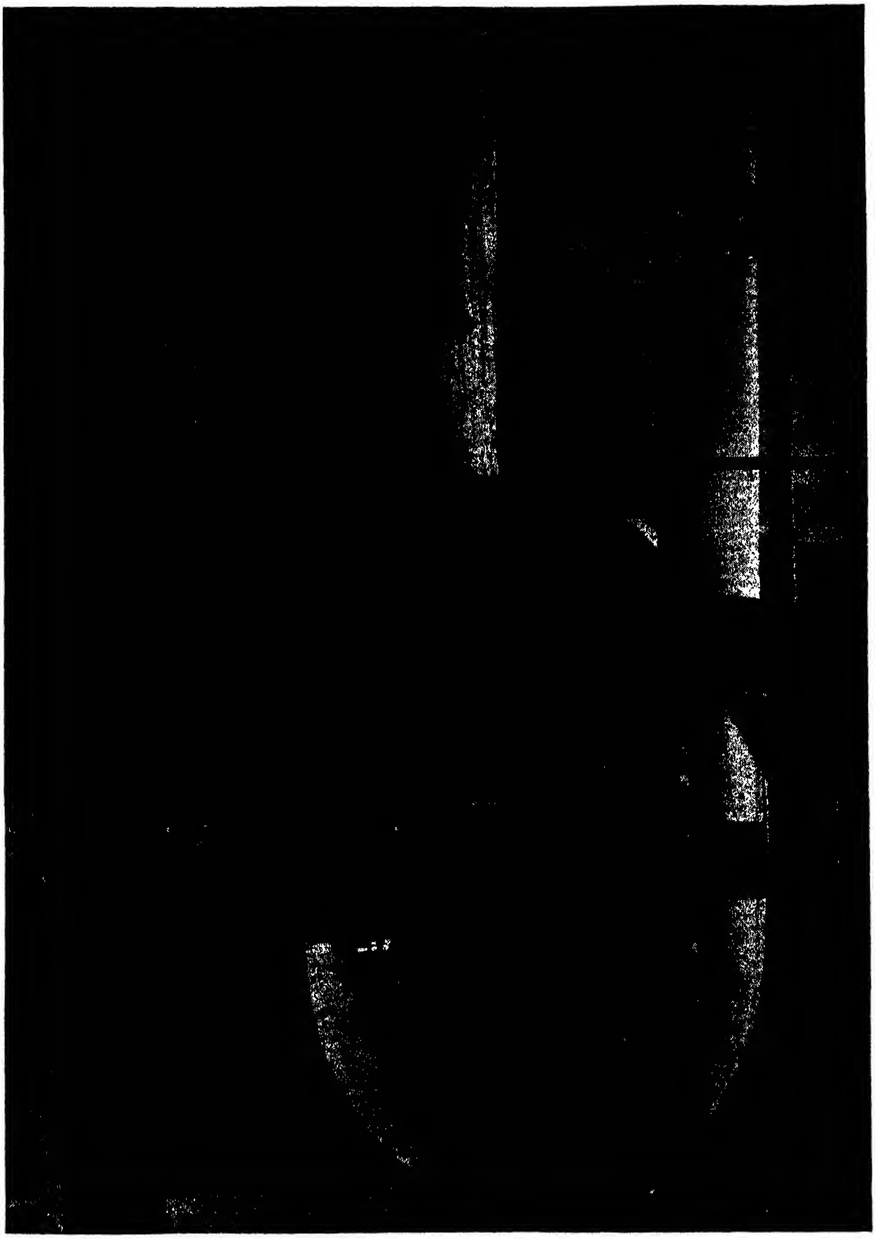

Fig. 4. Base of Ammonia Synthesis Bomb.

more or less common to all types of synthetic process irrespective of the source of the hydrogen and nitrogen. At best, modifications involving additional purification are sometimes inserted where the gaseous mixture is not of extreme purity.

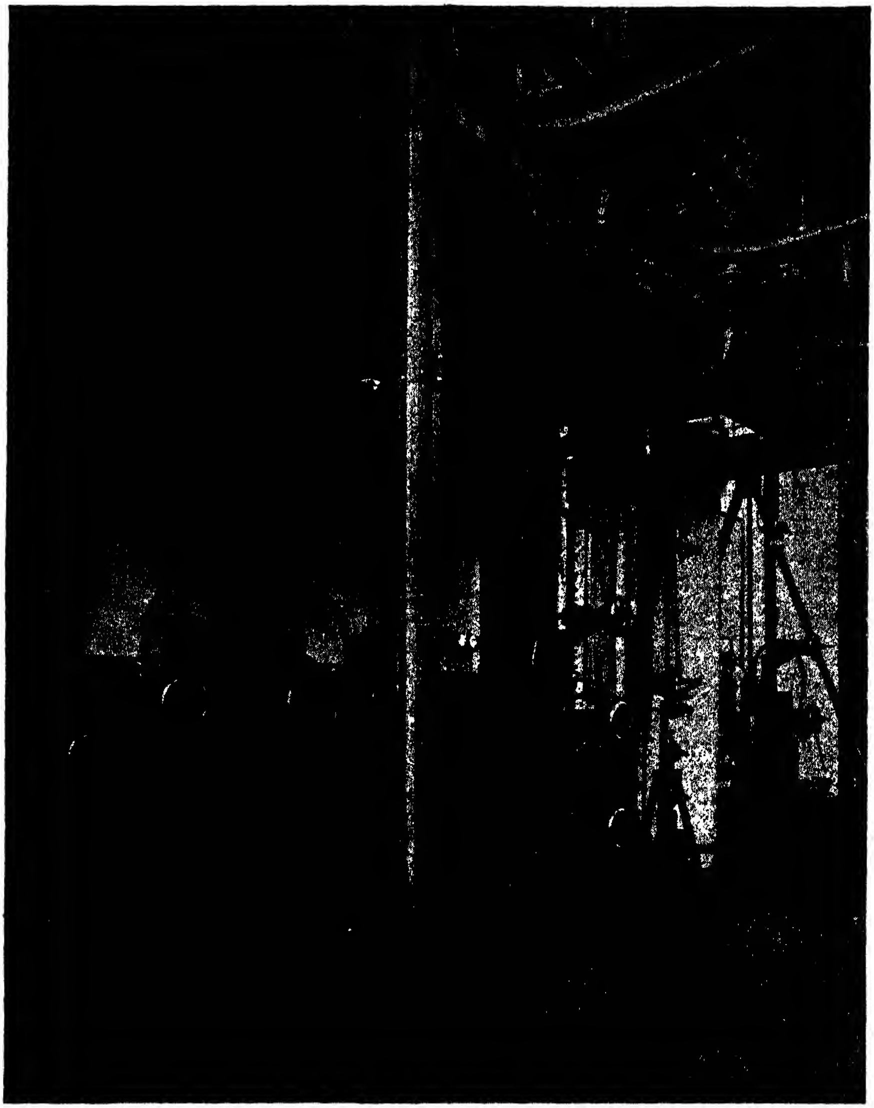

FIG. 5. Control Apparatus for Regulating Gas Flows.

Figure 4 shows the base of a catalytic bomb used in the synthesis of ammonia and illustrates the arrangement and type of piping and fittings used in this high-pressure apparatus. This particular bomb was operating at 300 atmospheres pressure. Figure 5 shows the general control apparatus for regulating the gas stream to the catalytic bomb. To the right is shown the receivers and separators which remove the ammonia from the gas stream leaving the bombs. All of this apparatus operates under a pressure above 300 atmospheres.

Compressors capable of developing the very high pressures and handling the large quantities of gases have offered no unusual problems to the compressor designer. However, the piping and valves, catalysts bombs, and circulating pumps have all involved new principles of design,[13] the working and shaping of new metals, and are of most massive construction.

Modifications of the Haber Process—The better-known modifications go under inventors' names. They will be discussed briefly.

Claude Process—The Claude process uses pressures up to 1000 atmospheres, and instead of recirculating the uncombined gases, it passes them through a series of catalyzers. Under this high pressure much larger proportions of the gases are combined on each pass. Claude has also developed a system of producing hydrogen by liquefaction and rectification of coke-oven gas, removing the hydrogen, which is purified by scrubbing with liquid nitrogen, and returning the methane to the gas mains.

Casale Process—In the Casale process pressures of around 700 atmospheres are used. Ordinarily the hydrogen is produced by the electrolysis of water, thus eliminating expensive purification operations. By using a more effective catalyzer, which means a more sensitive one, as much as 25 per cent of his gases are converted to ammonia in one pass through the catalyzer. To hold down temperatures in the catalyzer where such a high concentration of ammonia is maintained, he condenses out only a part of his ammonia and maintains a ballast on his heat-producing reactions by carrying a considerable quantity in his recirculating cycle. Under the pressures used in the Casale process, liquid ammonia can be condensed without difficulty, and with the usual cooling water it is easy to remove a part of the ammonia in this manner, and maintain a heavy circulation of ammonia in the apparatus by differential condensation. For temperature regulation, an electrical heater is used in the catalytic apparatus.

Fauser Process—The Fauser process is similar to the Casale process, working at a lower pressure and using electrolytic hydrogen. Fauser does not carry the excessive circulation of ammonia to maintain temperatures and his pressures are not high enough to condense out liquid ammonia with ordinary cooling water. He supplements his condensation apparatus by cooling through expansion of some of the liquid ammonia recovered.

The Mont-Cenis Process—This process operates at a low pressure, around 100 atmospheres, using an extremely active catalyzer.

The General Chemical Process—The General Chemical process is similar to the Haber process, using a pressure of about 125 atmospheres and a somewhat more sensitive catalyzer. Hydrogen is produced from water gas and the purification system is more elaborate because of the more sensitive catalyzer.

Energy Consumption in Ammonia Synthesis—The energy required for ammonia production depends largely upon the methods used to obtain nitrogen and hydrogen. The choice of methods is governed entirely by the available raw materials. Where hydroelectric power is cheap it can be used to the exclusion of all other forms of energy. A synthetic ammonia process uses for production of

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[13] See Chapter 4.

electrolytic hydrogen and the mechanical power in the plant, between 14,000 and 15,000 KW. hours per short ton of nitrogen. Or one can turn to the other extreme in which coke is the raw material for the production of hydrogen and nitrogen and the mechanical power is derived either from steam or gas engines. In this case if we reduce the coke into terms of its original coal and add to it the coal needed for mechanical power, such a synthetic process will require about 7 tons of high-grade American coal per short ton of nitrogen fixed. In the case of the processes using coke-oven gas, it is not quite so simple to evaluate the energy, for more frequently electric power is purchased for the motors, and coke-oven gas as the source of hydrogen.

Miscellaneous Fixation Processes—During the past seventy-five years a number of other processes for the fixation of atmospheric nitrogen, all of them related to the old barium cyanide process, have come into existence, operated for a few years, and disappeared. Millions of dollars have been invested in them, most of which has been lost. The underlying principle upon which they are based is that of passing nitrogen or reducing gases containing nitrogen over alkali carbonates. Mixed with the alkali salts are various forms of carbon, along with some catalytic material, usually oxide of iron. Various types of furnaces have been employed, in America rotating nichrome or nickel retorts; in Holland vertical iron tubes; in Sweden electric resistance furnaces. The products formed are alkali cyanides mixed with unreacted raw materials and catalytic agent. Although proposed as nitrogen fixation processes designed to make fertilizer nitrogen, none of them has progressed beyond the stage of furnishing small amounts of the higher-priced cyanides and ferrocyanides before the financial collapse.

At present it appears quite certain that the nitrogen fixation industry will rely permanently upon ammonia synthesis and the Cyanamid process for certain specialized nitrogen compounds.

NITRIC ACID

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Among the acids employed in chemical industry, nitric acid is second only to sulfuric in value and diversity of uses. The production in the United States was 176,000 tons HNO_3 in 1937[14] and greatly exceeded this figure in 1940. The technical grades of weak nitric acid (usually 50 to 60% HNO_3 by weight) are transported in stainless steel tank cars and in glass carboys, and C.P. acid, usually 70% HNO_3, is distributed in glass bottles. Concentrated nitric acid, normally 95% HNO_3, is delivered as such in stainless steel tank cars and in stainless and aluminum drums, and as mixed acid (nitric and sulfuric) in iron tank cars and drums.

[14] U. S. Dept. of Commerce, Biennial Census of Manufacturers (1937).

Uses—Nitric acid is a nitrating agent and an oxidizing agent, and its various uses depend on one or both of these characteristics. Most of the nitric acid produced is converted into nitrates and nitro-compounds, which in turn are employed as explosives,[15] fertilizers,[16] dyestuffs intermediates,[17] nitrocellulose plastics[18] and paints,[19] solvents, etc. Among the nitrates and nitro-compounds manufactured industrially with nitric acid are the following:

1. *Inorganic nitrates:* sodium nitrate, ammonium nitrate, calcium nitrate, lead nitrate, barium nitrate, strontium nitrate, copper nitrate, silver nitrate, mercuric nitrate.
2. *Organic nitrates:*[20] nitroglycerin (glycerol trinitrate), nitroglycol (glycol dinitrate), various grades of nitrocellulose (cellulose nitrate), nitrostarch, pentaerythritol tetranitrate, nitromannite (mannitol hexanitrate), etc.
3. *Organic nitrocompounds:*[20] nitrobenzene, dinitrobenzene, mono-, di-, and tri-nitrotoluene, tetryl, picric acid, trinitroxylol, nitrourea, nitromethane, etc.

Other uses of nitric acid depend, in part at least, on its oxidizing characteristics. Some of these are given below:

1. Manufacture of mercury fulminate
2. Pickling of steel and stainless steel
3. Pulping of wood[21]
4. Manufacture of anthraquinone from anthracene
5. Treatment of glass to produce a high-silica product[22]
6. Production of oxalic acid from molasses and other organic raw materials[23]
7. Production of glyceric, adipic, and glutaric acids from glycerol, cyclohexanol, and cyclopentanol, respectively[24]
8. Etching of engravers' plates

METHODS OF MANUFACTURE

Three methods of manufacture are or have been of real industrial importance in the manufacture of nitric acid: the soda nitric, the arc, and the ammonia oxidation processes. In the soda nitric process, sodium nitrate and sulfuric acid are heated in retorts,[25] and nitric acid, formed by the reaction:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

is distilled out of the retort and condensed. This process produces strong nitric acid, over 95% HNO_3 if desired, at high yields, and was without a serious com-

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[15] See Chapter 32.
[16] See Chapter 13.
[17] See Chapter 28.
[18] See Chapter 31.
[19] See Chapter 25.
[20] For the principles involved in the formation of these compounds see Chapter 3.
[21] Benson, H. K. and Walton, A. T., Paper Trade Journal, *111*, No. 10, 27-30 (1940); Aronovsky, et al., Paper Ind. & Paper World, *21*, 972-7 (1939).
[22] Chem. & Met. Eng., *46*, 444 (1939).
[23] Chem. Trade Journal, *105*, 239 (1939) and numerous patents.
[24] German Pat. 605,307; Aronow, A. M., U. S. Pat. 2,191,786 (1940); Perkins, R. P. U. S. Pat. 1,960,211 (1934).
[25] See also Chapter 9.

petitor in any country until 1913, when large arc process plants were put into operation in Norway.

In the arc process, air is passed through electric arcs, which cause the oxygen and nitrogen to combine to nitric oxide,[26] NO. This gas is cooled and permitted to oxidize to NO_2, before it is absorbed in water or alkalies to form nitric acid, alkaline nitrites, or nitrates. The concentration of the nitric oxide is low, 1 to 2%, the strength of the acid produced is only about 35% HNO_3, and the power costs and investment costs are high. In the ammonia oxidation process, ammonia and air or oxygen react in the presence of a catalyst to produce NO in a concentration of about 10%, which is then treated in a manner similar to that employed with gases from the arc process furnaces, but in smaller equipment, due to the greater concentration. The acid strength from ammonia oxidation plants is generally 50-65% HNO_3.

Historical Development—The development of synthetic nitric acid was accelerated by the War of 1914-1918. At the start of that war, practically all of the world's requirements of nitric acid were obtained by reacting sodium nitrate with sulfuric acid. A small industrial plant for the manufacture of nitric acid by the oxidation of by-product ammonia had been built in Germany in 1908 under the supervision of W. Ostwald, and the first European plants for producing nitric acid from air by the arc process had been erected in Norway at Notodden in 1905 and near the powerful Rjukan waterfalls in 1912 and 1913. An American arc process plant had been built in 1902 at Niagara Falls, but the plant was found to be uneconomical and was abandoned. The production by these two processes for the synthesis of nitric acid was negligible in 1914. A few months after the outbreak of the War it was realized in Germany that the predictions of a short war would not be fulfilled. Access to Chile nitrate was cut off and huge quantities of nitric acid from other sources were urgently needed. The arc process was considered impracticable under German conditions, so, with the exception of one small arc process plant, the Ostwald process of ammonia oxidation was adopted for the manufacture of sodium nitrate and nitric acid. Ammonia was available from by-product coke ovens, cyanamide plants, and especially from plants operating the then new Haber-Bosch process for pressure synthesis from nitrogen and hydrogen.

During the war period 1914-1918, considerable work on the production of synthetic nitric acid was carried out in all industrial countries, but nearly all of the nitric acid manufactured by all belligerents not subjected to the Allied blockade was derived from Chile nitrate. Two ammonia oxidation plants operated more or less successfully in England and France, making nitric acid by the Ostwald process mainly from ammonia from synthetic cyanamide, but the quantity of acid produced was small. Development in the United States was more energetic. An arc process plant for the production of sodium nitrite was erected at La Grange, Washington, in 1917, and several plants for the oxidation of by-product and cyanamide ammonia were built in the period 1916-1919. Including the two enormous Government plants at Muscle Shoals and Sheffield, Alabama, the capacity of ammonia oxidation plants completed or nearly complete by the

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[26] See p. 323.

spring of 1919 was said to be 225,000 tons of HNO_3 per year. However, these U. S. Government plants were shut down after a few weeks of operation.

After the Armistice in 1918, the ammonia oxidation process did not compete with soda nitric for several years, except in Germany. Chile nitrate was a cheaper raw material for the manufacture of nitric acid than by-product ammonia or ammonia from calcium cyanamide. In Germany, the synthetic ammonia process was supplying high purity ammonia at low cost, but this process was not operating in other countries. Experimental and development work continued, however, and from 1924 to 1930 synthetic ammonia plants were erected in over a dozen countries. Then the manufacture of nitric acid by oxidation of synthetic ammonia rapidly out-distanced the soda nitric process in volume. Even though these developments have forced the price of Chile nitrate from $2.50 to $1.35 per 100 lbs. f.o.b. Atlantic Seaboard, ammonia oxidation is supreme in the manufacture of nitric acid.

THE SODA PROCESS AND THE ARC PROCESS

Although of minor importance today, the soda nitric process is still operated in a limited number of plants throughout the world. In the United States, for example, several thousand tons per year of nitric acid are manufactured by this process in plants whose replacement by ammonia oxidation units has not appeared economical, due to special local conditions. However, for new installations, the ammonia oxidation process is selected. Moreover, very large quantities of synthetic sodium nitrate of high quality are manufactured in the important industrial countries from nitric acid or oxides of nitrogen obtained by the oxidation of ammonia. It is stated[27] that the production of synthetic sodium nitrate in the United States in recent years may have reached 450,000 tons per year. Because of the decline in the number of soda nitric plants, and the availability of descriptions of this process (see Reading List), details of this method of manufacture will be omitted.

The arc process is no longer of commercial importance, even the large Norwegian plants at Rjukan having been converted over to ammonia oxidation.

THE AMMONIA OXIDATION PROCESS

In the conversion of ammonia to nitric acid three reactions are involved:

$$(1)\quad NH_3(g) + 1\tfrac{1}{4}O_2(g) \rightarrow NO(g) + 1\tfrac{1}{2}H_2O(g) + 54.1 \text{ kg. cal.}$$

$$(2)\quad NO + \tfrac{1}{2}O_2 \rightarrow NO_2(g) + 13.6 \text{ kg. cal.}$$

$$\text{and}\quad (3)\quad 3NO_2(g) + H_2O(l) \rightarrow 2HNO_3 \text{ (50\% soln.)} + NO(g) + 29.4 \text{ kg. cal.}$$

A mixture of gaseous ammonia and air containing around 10% NH_3 by volume is passed through a catalyst where the first reaction occurs at a catalyst temperature of 700 to 930° C. with the evolution of NO and a large quantity of heat. This reaction takes place irreversibly on the catalyst of platinum group metals or base metal oxides. It is very rapid, less than 0.001 second contact time being

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[27] U. S. Tariff Comm., The European War and U. S. Imports (1939).

required in standard industrial plants operating with platinum or platinum-rhodium catalyst. Reaction (1) as written above gives the overall equation but does not reveal the mechanism. Extensive research has been carried out and some possible intermediates have been isolated in laboratory oxidation experiments under high vacuum,[27a] but the mechanism has not been established with certainty.

The second equation represents a reversible, homogeneous gas phase reaction. At temperatures above 400° C., little NO_2 can be formed, while below 100° C., the oxidation of NO to NO_2 is essentially 100% at equilibrium. Not only is the equilibrium of reaction (2) more favorable at lower temperatures, but the reaction rate increases with decrease in temperature. This peculiarity of the oxidation of NO to NO_2, namely, increase in rate with decrease in temperature, has been explained on the assumption that N_2O_2, a possible polymer of NO, is the intermediate compound. Regardless of the mechanism the rate of oxidation can be calculated from the data of Bodenstein.[28] This rate depends on the temperature of the gas and on the partial pressures of NO and oxygen.[29] In reaction (3), in which NO_2 and water form nitric acid and NO, the rate is relatively high and equilibrium is the controlling factor. Based on equilibrium measurements[30] and the performance of industrial plants, it is known that the maximum acid strength of the usual ammonia oxidation plants is limited to about 55% for atmospheric pressure and 67% for 100 lbs. per square inch pressure operation. The presence of NO tends to drive reaction (3) to the left, decomposing nitric acid back to NO_2 and water. It is essential, therefore, that the nitric oxide formed be reoxidized to NO_2. The size of absorption towers depends more on the rate of this reoxidation than on the absorption of NO_2 or the reaction of NO_2 with water.

Pressure Operation—It is apparent from the preceding section that a high partial pressure of NO and of oxygen is desirable to increase the strength of the acid produced and to reduce the size of the absorption towers. In the first ammonia oxidation plants ammonia was oxidized with air and all the reactions were carried out at atmospheric pressure. Later developments took two paths: increase in operating pressure and replacement of part or all of the air by oxygen. Plants employing oxygen were developed and built by the Bamag people in Germany and by Fauser in Italy, while the pressure process (100 lbs./sq. in.) was developed in the United States by du Pont.[31] Both developments gave an increase in acid strength and a decrease in equipment size and cost. For most localities the use of oxygen has proved uneconomical, but the 100-lb. pressure process has been adopted widely in the United States, Canada, England, South Africa, and some places in Continental Europe. However, the standard atmospheric plant is extensively used and is by no means extinct.

Pressure ammonia oxidation plants are employed in the United States by several important manufacturers of nitric acid. The increase from atmospheric pressure to around seven atmospheres results in an increase in acid strength of

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[27a] Bodenstein, M., Trans. Electrochem. Soc., *71*, 353 (1937).

[28] Bodenstein, M., Zeit. Phys. Chem., *100*, 105 (1922).

[29] Curtis, H. A., "Fixed Nitrogen," p. 385, Reinhold Pub. Corp., N. Y. (1932).

[30] Chambers, F. S. and Sherwood, T. K., Ind. Eng. Chem., *29*, 1415 (1937).

[31] Taylor, G. B., Chilton, T. H. and Handforth, S. L., Ind. Eng. Chem., *23*, 860 (1931).

nearly 15%, a 50-fold increase in the rate of reaction (2), and an even greater decrease in the tower volume required for oxidation and absorption.

One type of pressure ammonia oxidation plant is illustrated by the flow sheet of Figure 6. Anhydrous ammonia is vaporized, mixed with filtered, hot compressed air to a composition of about 10% NH_3 by volume, and the mixture is passed through the catalyst, which consists of a pad of several sheets of 90% platinum-10% rhodium alloy gauze. The ammonia is converted to nitric oxide at an efficiency of 95% or better. The hot gases, containing NO, water vapor, nitrogen, and a small amount of oxygen, leave the catalyst at temperatures approaching 900° C., and are subsequently cooled to 20-30° C. in heat exchangers and a cooler-condenser. In the latter piece of equipment, the water of reaction is condensed and removed as dilute nitric acid; the gas temperature is reduced to the desired point, and the NO is oxidized to NO_2. The gas then enters the bottom of the absorption tower. The dilute nitric acid from the cooler-condenser enters the tower at a higher point, and pure water is introduced at the top. Nitric acid at a strength in excess of 60% HNO_3 flows continuously from the tower through the bleacher into scale or storage tanks. Auxiliary air passes through the bleacher, where it removes from the acid any dissolved oxides of nitrogen, into the absorption tower to supply the oxygen required to reoxidize the NO formed within the tower by reaction (3). The heat generated within the tower is removed by cooling coils. The waste gas, containing nitrogen, a few per cent of oxygen, and a fraction of a per cent of NO_2, is reheated and expanded through expansion engines to atmospheric pressure. The power recovered from expan-

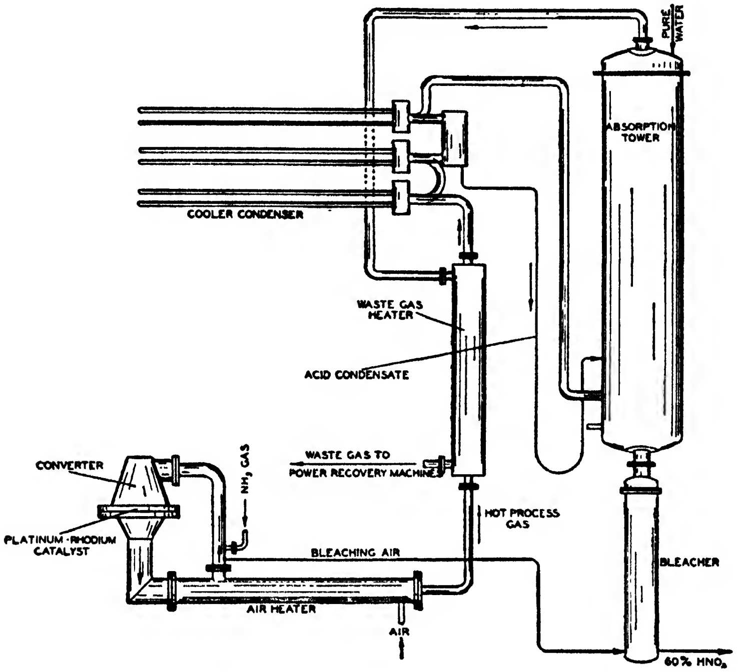

FIG. 6. Pressure Ammonia Oxidation Plant.

sion engines and waste heat boilers is sufficient to compress approximately one-half of the air required by the process.

Catalysts and Converters—Ammonia may be oxidized to nitric oxide, nitrous oxide, or nitrogen, depending on the catalyst, temperature, and contact time. These equations are:

$$NH_3(g) + 1\frac{1}{4}O_2(g) \rightarrow NO(g) + 1\frac{1}{2}H_2O(g) + 54.1 \text{ kg. cal.} \quad (1)$$

$$NH_3(g) + O_2(g) \rightarrow \frac{1}{2}N_2O(g) + 1\frac{1}{2}H_2O(g) + 65.9 \text{ kg. cal.} \quad (4)$$

$$NH_3 + \frac{3}{4}O_2 \rightarrow \frac{1}{2}N_2 + 1\frac{1}{2}H_2O + 75.7 \text{ kg. cal.} \quad (5)$$

For the manufacture of nitric acid, Equation (1) is the desired one, although Equation (5) is known to occur when certain catalysts or operating conditions are employed. The reaction of Equation (4) has been suggested[32] as a method of preparing nitrous oxide, but there is some doubt if it has ever been adopted in practice.

Platinum and Platinum Alloys—For the oxidation of ammonia to NO, there are two important groups of catalysts—platinum metals and base metal oxides. Platinum is the original catalyst of W. Ostwald, and is still in use in a number of plants, but it has been replaced widely in the major industrial countries by an alloy of platinum and rhodium. This alloy, containing 1½ to 10% rhodium, was adapted for this use in the United States in 1928.[33] In spite of numerous binary, ternary, and quaternary alloys of platinum, rhodium, iridium, ruthenium, etc., that have been suggested and tested,[34] platinum-rhodium is without an equal in giving high conversion efficiency and low catalyst loss, which for atmospheric pressure operation on ammonia-air mixtures, are given below:

Efficiency and Loss Data on 90% Pt-10% Rh Alloy[34]

Temperature of Catalyst, °C.	835	900
Conversion Efficiency, %	97	99
Catalyst Loss, Troy oz./100,000 lb. NH_3 burned	0.2	0.55

At higher pressures there is a moderate reduction in conversion efficiency and an increase in catalyst loss.

The platinum metal catalysts are changed in physical structure by the part they play in the oxidation of ammonia. The wires of unused gauze are smooth and shiny, but in the converter the gauze soon becomes dull in appearance. Under the microscope, it is seen that each wire is covered with nodules of the metal (Figure 7), and the surface and outside diameter of the wire have increased. This "sprouting" continues throughout the life of the gauze—that is, until loss of metal and mechanical strength makes replacement advisable. Part of the metal that has disappeared from the gauze is removed from the gas stream at points downstream of the converter and may be recovered as dust and refined.

Platinum and platinum-rhodium catalysts are employed in the form of gauze, the 80-mesh by 0.003" wire being the favorite in this country. The size of the sheets and their arrangement vary greatly in different plants. On the continent of Europe, the Bamag type of converter is widely used, with a two-layer circular

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[32] Schlecht, L. and Nagel, A. v. U. S. Pat. 1,946,114.
[33] Davis, C. W., U. S. Pats. 1,706,055 (1929) and 1,850,316 (1932).
[34] Handforth, S. L. and Tilley, J. N., Ind. Eng. Chem., *26*, 1287 (1934).

gauze pad up to 2 meters in diameter, the ammonia-air mixture traveling vertically upward. The United Alkali converters, with small rectangular gauze pads of 3 to 4 layers, are well known in England.[35] The multi-layer gauze, with 10 to 30 sheets per pad, was developed in the United States[36] for atmospheric and pressure operation. This type of gauze is normally employed without the gauze holder usually found in United Alkali or Bamag type converters. In converters designed for the multilayer gauze, the gas travels downward through the catalyst and the gauze pad is supported by a heavy screen beneath it (Figure 8). As the gauze becomes worn and metal is lost, new sheets may be added and worn fragments removed for recovery of the precious metals. The Parsons converter[37] was outstanding in the United States at one time and was installed in the Muscle Shoals plant, but it has in general been superseded by more modern designs. This converter consists of a vertical cylinder of three or four layers of platinum or platinum-rhodium gauze, closed by a circular plate of silica. The gauze is suspended in a brick-lined converter. The ammonia-air mixture enters the cylinder at the top and flows radially outward through the gauze. Heat radiates from the catalyst to the refractory brick and back to the catalyst to hold the gauze at the desired high temperature, thereby eliminating the electric heat required by some of the earlier converters to hold the catalyst temperature at the optimum level. Modern flat-gauze converters, however, operate with preheated air, and require neither electric heat nor refractory brick to prevent undue loss of temperature.

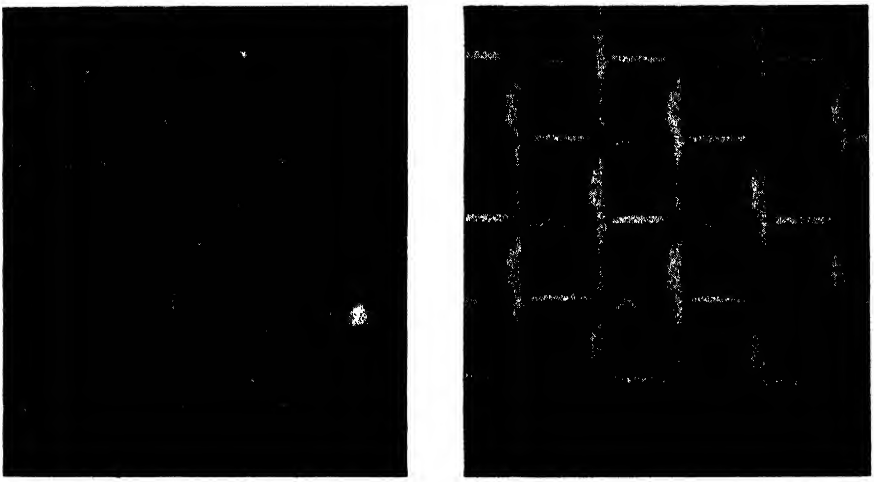

FIG. 7. Photomicrograph Platinum-Rhodium Gauze After Use and Before Use.

Where ammonia is burned with oxygen, as is done in some plants in Europe, special converters are required. The absence of nitrogen to dilute the mixture of ammonia and oxygen and to absorb 70% of the heat generated by the reaction would lead to gas explosions and to such high temperatures that the catalyst

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[35] Imison, C. S. and Russell, W., J. Soc. Chem. Ind., *41*, 37T (1922).
[36] Handforth, S. L. and Kirst, W. E., U. S. Pat. 1,919,216 (1933).
[37] Curtis, H. A., op. cit., p. 378.

would be melted. Therefore, steam is generally employed in the absence of nitrogen as a diluent. This excess water vapor, together with that formed in the reaction, is removed with little nitric acid by rapid cooling of the gases leaving the converter and withdrawal of water before any appreciable amount of NO_2 has formed.

Other types of converters for handling ammonia-oxygen mixtures include that of Cederberg,[38] which is designed to prevent explosions and to remove the heat of reaction by cooling the catalyst. Where the air is not displaced by oxygen, but only enriched with it, and the ammonia concentration in the gas mixture does not exceed about 12% by volume, standard converters for ammonia-air may be used.

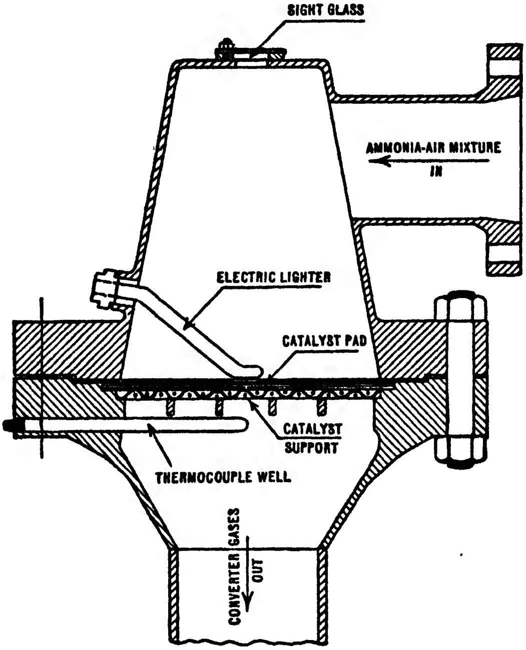

FIG. 8. Ammonia Oxidation Converter.

Operating Conditions. Economical operation of a converter demands high efficiency in the conversion of ammonia to nitric oxide, low catalyst cost, and high capacity. The factors affecting these items, such as ammonia purity and concentration, ammonia rate, composition and quantity of the catalyst employed, temperature of the catalyst, time of contact, operating pressure, and oxygen concentration, are so interrelated that no standard set of operating conditions is satisfactory for all plants. Nevertheless, the more important are discussed briefly.

Efficiency of Conversion. High purity ammonia and clean air are necessary for high efficiency. Although by-product ammonia and cyanamide am-

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[38] Cederberg, I. W., U. S. Pat. 1,859,863 (1932). See also Fischer, T. and Wendlandt, R., U. S. Pat. 1,850,129 (1932).

monia can be purified satisfactorily, high-grade synthetic ammonia is considered the best raw material for nitric acid plants.

Platinum-rhodium, with 2 to 10% rhodium, depending on the temperature employed, gives the highest conversion efficiency and lowest catalyst loss. In the usual form of gauze of about 80 × 80 mesh × approximately 0.003″ diameter wire, the quantity of catalyst in an atmospheric pressure converter may vary from 1 to 3 ounces per 100 lbs. ammonia fed to the converter daily. The contact time is usually less than 0.001 second. For optimum operation in pressure converters the amount of catalyst in a converter is lower than that in an atmospheric converter of equal capacity. Roughly, the amount of catalyst per 100 lbs. ammonia daily capacity is varied inversely as the absolute pressure. The time of contact is nearly independent of pressure.

The temperature of the catalyst as employed commercially may vary from 700° C. to slightly over 900° C. Since, within this range, both conversion efficiency and catalyst loss increase with increase in the temperature of the catalyst, the optimum temperature is selected only after a careful study of conversion and catalyst loss data and the costs of ammonia and catalyst. Some atmospheric pressure plants on the European continent are said to operate at gauze temperatures of about 700-750° C. Apparently these are plants using platinum or platinum alloys very low in rhodium, or plants employing oxygen or oxygen-enriched air in the converters. With platinum as a catalyst, the low gauze temperatures are desirable to avoid excessive metal losses. At high oxygen concentration, the conversion efficiency at temperatures around 750° C. may be sufficiently high to make the use of higher temperatures unwarranted. For mixtures of ammonia and air, however, 800° to 850° C. is the temperature range usually recommended for atmospheric converters, and even higher temperatures for pressure converters.

Base Metal Catalysts—As an alternative to platinum, base metal catalysts were employed in Germany during the first World War and are used now in localities where ammonia is very cheap or platinum and rhodium are scarce. Iron oxide and iron oxide promoted with bismuth oxide were used in early German plants.

Base metal catalysts consisting of cobalt oxide and aluminum oxide[39] as well as numerous other oxides have been recommended. Although such catalysts are employed to a considerable extent in the United States and elsewhere, their use is not so widespread as that of platinum and platinum-rhodium, and the published information is less complete.

Absorption Towers. The hot gases leaving a converter are cooled, and the water of reaction, containing some HNO_3, is condensed and separated from the gas. In plants operating at atmospheric pressure, the acidity of this condensate varies from about 2% to 30%, depending on the rapidity with which the gas is cooled and the water separated. Slow cooling permits the oxidation of a large part of the NO to NO_2, which in turn reacts with the condensate to form nitric acid. An increase in pressure increases the rate of oxidation and thereby increases the acidity of the condensate. This nitric acid is not lost, but the concentration of oxides of nitrogen in the gas fed to the absorption system is reduced and, as a result, the strength of acid in equilibrium with it is slightly lowered.

[39] Fogler, M. F., U. S. Pat. 1,936,936 (1933).

Oxidation of NO. Following the removal of the condensate, the gas is passed through oxidation chambers to permit the reaction

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 + 13.6 \text{ kg. cal.}$$

to proceed almost to completion. In plants under atmospheric pressure, several very large tanks or towers are required, while a few lengths of pipe may suffice for high pressure plants, since the volume required to permit any given degree of oxidation varies inversely as the cube of the pressure. The gas must be cooled to remove the heat of reaction and to hold the temperature low where the rate of oxidation is the greatest.

After the water is removed and the NO is oxidized to NO_2, the gas enters the absorption system where it is absorbed in water to form nitric acid. The flow of acid and gas is countercurrent. Pure water is introduced into the last tower, and the acidic condensate is fed into the tower having approximately the same concentration. In the older atmospheric plants, five to ten enormous packed towers of granite or acid-resisting brick were used, with acid circulating over each by means of air lifts. Some towers were over 50 ft. high and even 30 ft. in diameter. Later plants have stainless steel towers and stainless or high silicon iron pumps, but the large volumes have not been reduced. This large volume is needed to provide time to reoxidize to NO_2 the NO formed in the reaction

$$3NO_2(g) + H_2O(l) \rightleftarrows 2HNO_3 \text{ (50\% soln.)} + NO(g) + 29.4 \text{ kg. cal.}$$

The heat generated by the above reaction and by the oxidation of NO to NO_2 is removed by cooling the towers or the circulating acid. The anhydrous ammonia required by the plant may be used to advantage as a refrigerant for reducing the temperature of the acid in the strong end absorption towers below that possible with cooling water alone. This refrigeration increases the strength of the acid produced and the rate of oxidation of NO to NO_2.

In ammonia oxidation plants, the size of the absorption system decreases so rapidly with increase in pressure that, at about 8 atmospheres absolute, space for reoxidation of NO to NO_2 ceases to be the controlling factor in design. Stainless steel bubble-cap absorption towers with cooling coils on each tray (Figure 9) are then preferred over packed towers.[40]

A limited number of plants have been built which combine oxidation of ammonia and removal of water at atmospheric pressure, with pressure absorption of the resulting gases, stainless steel turbo compressors being installed to compress the gases before they enter the absorption system. This combination of atmospheric and pressure operation has not been adopted generally. It is possible that there were serious limitations to the compressor when operating on gases containing oxides of nitrogen.

Other Sources of Nitrogen Oxides—Oxides of nitrogen from sources other than ammonia oxidation converters are converted into nitric acid by absorption in water. Fumes from operations involving oxidation or nitration with nitric acid and gases obtained by denitrating nitroglycerin, nitrocotton, and TNT "spent acids" are treated at atmospheric pressure in absorption towers in a manner similar to that for ammonia oxidation gases. The oxides of nitrogen in the gases

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[40] Handforth, S. L., U. S. Pat. 2,019,533.

from spent acids are often in concentrated form, over 75% NO_2, and the acid strength obtainable and the necessary time for reoxidation of NO to NO_2 approach that of pressure plant rather than atmospheric operation. Therefore, a bubble-cap tower with trays about one foot apart and with cooling coils on each tray is sometimes more economical than a series of packed towers with circulating pumps. Single-pass packed absorption towers are less often selected, due to the relatively low liquid rate and the difficulty of control.

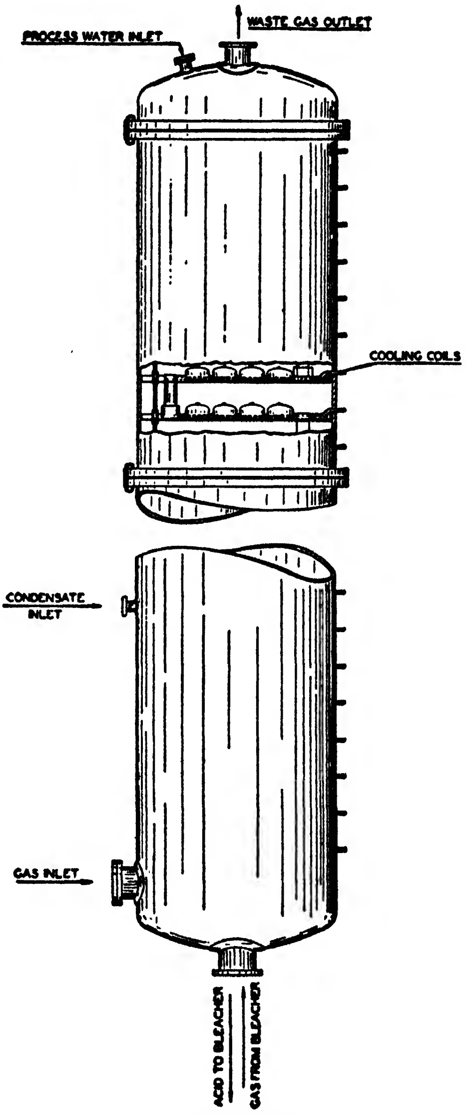

FIG. 9. Inner-cooled Absorption Tower.

Sodium Nitrate and Nitrite—Sodium nitrate and sodium nitrite are manufactured by absorbing the gases from ammonia oxidation converters in soda ash or caustic soda. The towers are similar in size and design to atmospheric pressure nitric acid absorbers.

Production of Strong Nitric Acid—Nitric acid produced by absorption of nitrous gases in water, as described in the preceding sections, does not exceed 65% HNO_3 in strength. These concentrations are satisfactory for the manufacture of inorganic nitrates and for the oxidation or nitration of some organic compounds, but for the manufacture of nitroglycerin, nitrocellulose, TNT, and a number of other compounds, stronger acid is required. Nitric acid of 90-98% HNO_3 is produced in large quantities by concentration of the weak acid from ammonia oxidation plants, and in much smaller quantities from liquid NO_2, weak nitric, and oxygen.

Nitric Acid Concentration—Weak nitric acid cannot be concentrated by simple rectification above 68% HNO_3, the constant-boiling mixture. Concentration of weak nitric acid to a strength of 90% HNO_3 and higher was not highly developed in 1915 when the large German ammonia oxidation plants were built. As a result, sodium nitrate, rather than nitric acid, was produced by some of the important oxidation plants, and the sodium nitrate was converted in soda stills to strong nitric acid. However, at the present time, concentration to 98% is readily accomplished industrially by boiling a mixture of weak nitric and strong sulfuric acid. The sulfuric acid holds the water and permits strong nitric acid to be distilled out and condensed. This concentration can be carried out in various types of equipment. Direct fired batch stills similar to those used for the soda nitric process were employed in many of the earlier plants for concentrating oxidation plant nitric. Several better processes have since been developed and widely adopted. First among these should be mentioned the Pauling concentrator,[41] a packed tower into which weak nitric acid and 92-96% sulfuric acid, or a prepared mixture of weak nitric and sulfuric acid, are fed in at the top and live steam is introduced at the bottom. Nitric acid vapors leave the top of the column and pass to a condenser, where 94-98% acid is obtained. A very small amount of oxides of nitrogen pass on to a water scrubber. Weak sulfuric acid, 70% H_2SO_4, leaves from the bottom of the packed tower, to be reconcentrated and re-used.

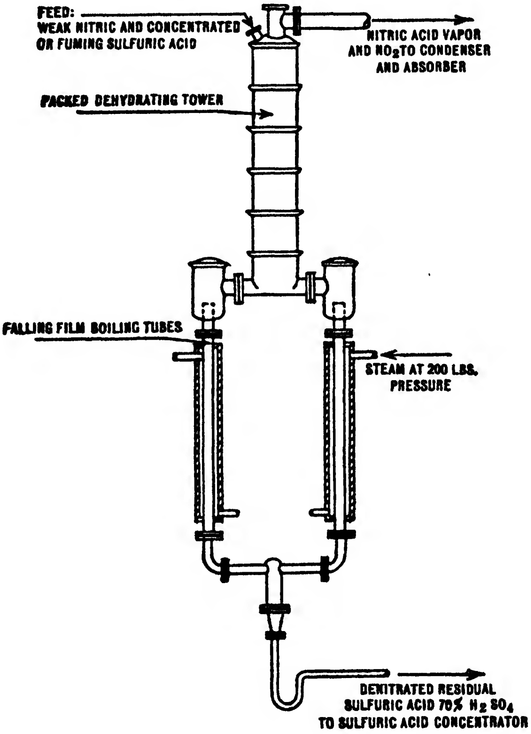

FIG. 10. Nitric Acid Concentrator.

Other types of nitric concentrators, described by Hechenbleikner,[42] by Davis, et al.,[43] and by Peterson, et al.,[44] employ a short packed tower, beneath which is a boiler of steam-jacketed tubes of high silicon iron. The Peterson concentrator is illustrated in Figure 10. Steam and nitric vapors are generated in the boiling

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[41] Pauling, H., U. S. Pat. 1,031,865 (1912).

[42] Hechenbleikner, I., U. S. Pat. 1,818,711 (1931).

[43] Davis, C. W., Handforth, S. L., and Kirst, W. E., U. S. Pat. 1,922,278 (1933).

[44] Peterson, R. F., and Wrightsman, P. G., U. S. Pat. 2,201,631 (1940).

tubes, and pass upward into the packed tower, countercurrent to the mixture of sulfuric acid and weak nitric acid. The steam condenses in the tower and boils off strong nitric acid. Since little or no live steam is introduced into the system, the steam consumption and the sulfuric consumption are less than those of the Pauling concentrator. In the Zeisberg concentrator,[45] only sulfuric acid is fed into the top of the packed tower; the nitric acid and much of the necessary heat is introduced as weak nitric vapor, obtained by boiling the weak nitric acid.

Strong Nitric from Liquid NO_2—Strong nitric acid of 90-98% HNO_3 can be produced directly from liquid NO_2, weak nitric acid or water, and oxygen under high pressure. The reaction,

$$2NO_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2HNO_3 \qquad (6)$$

is carried out at elevated temperatures, 60-100° C., and at oxygen pressures of approximately 1000 lbs./sq. in. Processes in which liquid NO_2 is separated from ammonia oxidation converter gas and subsequently reacted with weak nitric acid and oxygen under high pressure are described in a large number of patents. Several direct nitric plants have been erected, especially in Europe by the Bamag and the Fauser interests, but the standard ammonia oxidation process for the production of weak nitric, coupled with efficient concentration plants, have not been seriously threatened. It is possible that the cost of oxygen, and the corrosive nature of strong nitric acid at the elevated temperatures, combine to make these plants unattractive for many localities.

Materials of Construction—Many of the stainless steel alloys high in chromium or in chromium and nickel are very resistant to cold nitric acid of any concentration.[46] In fact, modern ammonia oxidation plants and nitric acid tank cars are constructed largely of these metals, since they combine good tensile strength and workability with corrosion resistance. Aluminum is satisfactory for cold, concentrated nitric but is less resistant to weak acid. For boiling nitric acid of any concentration, high silicon iron is the standard metal. The corrosion resistance is excellent, but the tensile strength is too low and the material is too brittle for many applications involving high pressure. Platinum, tantalum, glass, silica, porcelain, and some acid-resistant brick are resistant to nitric acid. Asbestos is probably the most widely applicable packing material, although some of the synthetic rubbers are satisfactory in cold, weak acid. Organic lubricants are incompatible with nitric acid, and, with concentrated nitric or with strong mixed acid, may be hazardous. Therefore, lubricants for stuffing boxes of pumps should be selected with care and used sparingly.

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[46] Maxwell, H. L., Trans. Am. Inst. Chem. Engrs., *35*, 159 (1939).

CHAPTER 9

NATURAL SALTS AND BY-PRODUCTS *

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Natural salt deposits constitute a tremendous source of world wealth. This wealth is widely distributed among nations and therefore is not, generally speaking, the object of international contest. Some of the less abundant salts, such as potash and nitrates, were once thought to be localized in Germany and Chile respectively. However, the World War of 1914-1918 stimulated exploration and exploitation, with the result that tremendous sources of potash have been revealed in the United States, Russia, Asia Minor and elsewhere. As for sodium nitrate, practically every country, large or small, ambitious for economic autonomy, now has its synthetic ammonia and nitric acid plants [1] and its Solvay Process soda plants, which do away with the necessity of having the natural material. Nitrogen is equally available to all and salt is practically in the same category. Nitrogen and salt are the basic raw materials of the modern nitrate industry.

Water soluble natural salts, the subject of this chapter, include chiefly the chlorides, bromides, iodides, sulfates, carbonates, nitrates and borates of the metals sodium, potassium, calcium and magnesium. The distribution of the less abundant salts is almost as widespread as that of sodium chloride itself, and no nation need suffer from a serious lack in its normal pursuit of agriculture and industry. It is true that there are other controlling factors in establishing chemical industry: the distribution of fuel—coal, oil, gas, water power; the distribution of other minerals—limestone, sulfur, phosphates, iron ore, heavy metals, and forest products; transportation facilities; climate. The nations are decidedly unequally provided with these items of wealth. For this reason the development and utilization of natural salts is greatest in the so-called industrial nations.

GEOLOGY OF THE SALT BEDS

The Sea as a Source of Salt—The reason for the widespread distribution of natural salts is not hard to find. The sea is responsible. The sea is a vast sink into which has poured the rivers of earth throughout geologic time. These rivers contain soluble matter extracted from the rocks of continental uplands by pluvial and volcanic waters. The steady cycle of evaporation from the sea, rainfall on the continents and return to the sea, has built up the salinity of the sea water to about 35 grams per liter. The estimated volume of the intercon-

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* Includes Salt, Magnesium Compounds, Bromine, Iodine, Natural Soda, Borax, Potash, Sodium Sulfate, Hydrochloric Acid, and Natural Sodium Nitrate.

[1] See Chapter 8.

nected salt water on earth is 1,330 million cubic kilometers, weighing 138×10^{16} metric tons. The estimated content of salts is 4.84×10^{16} metric tons. In volume this would give 21.8 million cubic kilometers, a quantity sufficient, if spread over a level sea bottom of 361 million square kilometers (the area of the sea surface), to make a layer more than 60 meters thick, and of this layer 47.5 meters thick would be common salt (NaCl).

The average composition of ocean salt, according to Dittmar,[2] is given in the following tables:

TABLE 1—ANALYSIS OF THE SALINE MATERIAL OF OCEAN WATER CALCULATED IN IONS

Ions	*Per Cent of Total Salts*	*Grams per Liter of Ocean Water*
Cl	55.292	19.68
Br	0.188	0.07
SO_4	7.692	2.74
CO_3	0.207	0.08
Na	30.593	10.89
K	1.106	0.40
Mg	3.725	1.33
Ca	1.197	0.43
Total	100.000	35.62

TABLE 2—ANALYSIS OF THE SALINE MATTER OF OCEAN WATER CALCULATED AS SALTS

Salt	*Per Cent of Total Salts*	*Grams per Liter*	*Short Tons per Cubic Mile*
NaCl	77.758	27.213	131,526,000
$MgCl_2$	10.878	3.807	18,399,000
$MgSO_4$	4.737	1.658	8,012,000
$CaSO_4$	3.600	1.260	6,089,000
K_2SO_4	2.465	0.863	4,170,000
$CaCO_3$	0.345	0.123	584,000
$MgBr_2$	0.217	0.076	367,000
Total	100.000	35.000	169,147,000

Besides the principal constituents noted in the tables there are smaller amounts of practically every known element in sea water.

The salinity of sea water in land-locked mediterraneans in warm climates may be higher, as in the Red Sea (38.8 grams per liter). It may be lower in other water bodies plentifully supplied with fresh water from streams or melting ice. Thus the Black Sea has a salinity of 22 grams per liter, and the Baltic decreases from full salinity in the North Sea to 10 grams per liter in the Finnish Gulf. These considerations are important in the direct recovery of salt, bromine, and magnesia from sea water by methods to be described.

Concentration by Living Matter—The living plants and animals of the sea have the ability to concentrate some of the rarer elements in their bodies, and this is also of importance to industry. For example, certain kinds of sea weed (*Laminaria digitata* and *L. stenophylla*) contain about 0.3 per cent of iodine on the weight of dry kelp, which serves as excellent raw material for iodine recovery. Many organisms, such as foraminifera, brachiopods, and coral, growing

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[2] Clarke, F. W., U. S. Geol. Survey Bull. 770, "The Data of Geochemistry," p. 203 (1924).

in shallow water, secrete lime, and the calcareous bodies form into reefs, and in time build up thick limestone deposits.

Connate Salt—Sedimentary deposits in general form on the ocean floor, from sand and clayey material carried down with the rivers. Sedimentary rocks are porous in varying degrees, ranging from 1.3 per cent for granite to over 20 per cent in some sandstones. Fossil sea water trapped in the pores gives rise to connate salts, which range from about 1 per cent by weight to as high as 8 per cent in some cases.

Vast areas of the continents now above sea level were at one time, or several times, submerged by the sea. Elevation of the land, or recession of the sea, has left the sedimentary rocks high but not dry. Erosion and solution by terrestrial waters again leach out the connate salts, and in addition yield other soluble material through decomposition. These salts may or may not be washed back into the sea. There are many valleys and basins in western United States where there is no outlet to the sea. The slightly saline rivers drain into land locked lakes where the salts are concentrated by evaporation. The Great Salt Lake in Utah lies in the deepest portion of the basin of a former great fresh water lake, Lake Bonneville. The lake is not a remnant of a cut-off portion of the sea, for the tertiary deposits which surround and underlie it are of continental origin. On the other hand, the composition of the salts in the lake water resembles closely that of sea water (see Table 3), and this seems to indicate that the origin of the salts was the connate salts in the surrounding terrain.

TABLE 3—COMPOSITION OF NATURAL BRINES, PERCENTAGE ON DRY BASIS

Body of Water	*Sea Water*	*Great Salt Lake, Utah*	*Salton Sea*	*Searles Lake, Cal.*	*Owens Lake, Cal.*	*Dead Sea*
Cl	55.29	55.48	47.83	37.04	25.56	65.86
Br	0.19	...	...	0.24	...	1.13
SO_4	7.69	6.68	13.41	13.00	9.96	0.39
CO_3	0.21	0.09	1.85	7.24	22.18	0.02
B_4O_7	...	...	...	2.50	1.92	...
Na	30.59	33.17	31.29	33.80	38.07	13.73
K	1.11	1.66	0.65	6.34	2.10	2.36
Mg	3.73	2.76	1.81	...	...	12.32
Ca	1.20	0.16	2.80	...	...	4.19
Sp. Gr.	1.025	Variable	Variable	1.297	Variable	1.156
Salinity	35.0	140–280	...	452	63–244	218–259
Date	...	1913	1907	1929	1912	1912
Source of Salt	...	Connate Sea Water	Chiefly Sea Water	Terrestrial	Terrestrial	Sea Water & Terrestrial

Deposition of Salt from Sea Water—In order to give an insight into the diversity of character of saline deposits throughout the world, and to indicate how the various constituents may be separated in industry as well as in nature, it is desirable to present a brief discussion of the geological features of the salt deposition.

A body of sea water, more or less isolated from the circulating ocean currents, will concentrate when the climatic conditions are such as to cause a greater amount of evaporation of water than is supplied by precipitation, by affluents, or by springs. These conditions exist in many parts of the world today, and the huge deposits of sea salt in older geologic strata are eloquent evidence that such conditions have existed in the past.

When sea water is evaporated no salts are deposited until the salinity reaches 72 grams per liter, at which point $CaCO_3$ and Fe_2O_3 begin to precipitate. When the volume is reduced to 19 per cent and the salinity to 202 grams per liter, $CaSO_4 \cdot 2H_2O$ begins to separate, and this continues until it is exhausted at 3 per cent of the original volume. Sodium chloride begins to precipitate when the volume is reduced to 9.5 per cent, when the salinity is 388 grams per liter and the density is 1.21, and continues until the solution is dry. $MgSO_4$ begins to precipitate when the volume is reduced to 1.66 per cent, when the salinity is 523 grams per liter and the density is 1.32. (See Figure 1.)

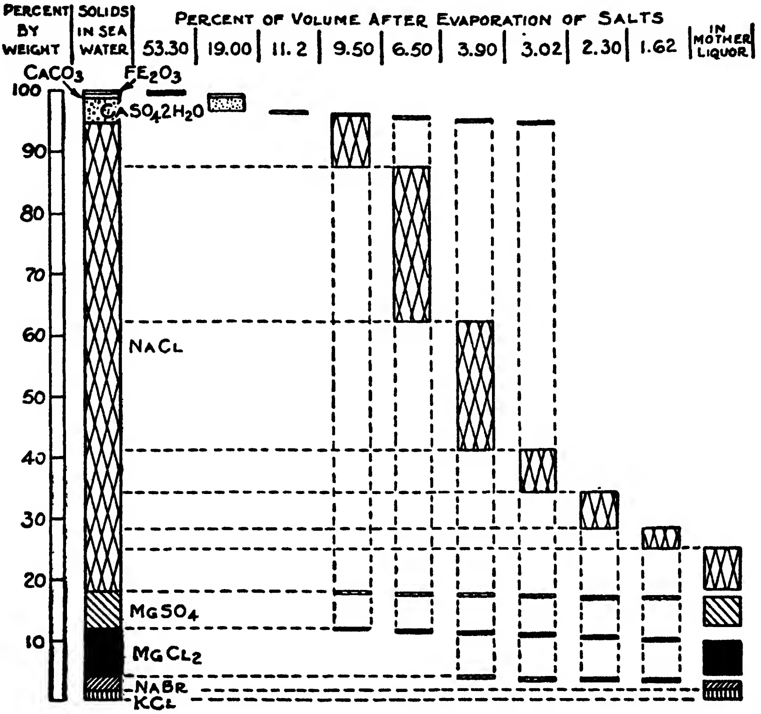

FIG. 1. Diagram Showing Order of Separation of Salts. [Alling, H. A., New York State Mus. Bull. 275, p. 81 (1928)]

This diagram shows the order of the separation of salts on evaporation, under atmospheric pressure, of sea water. The dry salts, per cent by weight, calculated to be in sea water are given at the left. The percentage of each salt which separates as the volume of the solution is reduced by evaporation is shown in the succeeding columns. That is, when the volume has been reduced to 53.30 per cent of the whole, a little ferric oxide and calcium carbonate has crystallized. At 19 per cent the rest of the calcium carbonate and some of the gypsum have separated, and so on. If all of the "blocks" of these columns should be shoved together they would reconstruct the first column. Note that at no time is pure sodium chloride precipitated without some other salt.

From this point on the mother liquor will deposit a succession of complex salts, depending on the temperature, and depending on whether the salts are left in contact with the mother liquor. At 25° C., van't Hoff found the following order for the separation of mother liquor salts, always in company with sodium chloride: (1) magnesium sulfate, (2) magnesium sulfate and kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$), (3) hexahydrate ($MgSO_4 \cdot 6H_2O$) and kainite, (4) kieserite ($MgSO_4 \cdot H_2O$) and kainite, (5) kieserite and carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$), (6) kieserite, carnallite and bischofite ($MgCl_2 \cdot 6H_2O$). The temperature at which the mother liquor salts were actually laid down was probably around 50° C., because shallow saline lake water is known to absorb visible solar radiation and to get quite hot. At this temperature the order of deposition would be loewite ($Mg_2Na_4(SO_4)_4 \cdot 5H_2O$) at 3.3 per cent of the original volume of sea water, then langbeinite $Mg_2K_2(SO_4)_3$, kieserite and finally carnallite.

In nature no orderly succession of deposits in a single locality is possible. There were many interruptions in the process of evaporation. There were successive transgressions and recessions of the sea, due to periodic land movements. There were many climatic cycles, alternate wet and dry periods, alternate hot and cold. Irregular uplifts or sinking of land would transfer the mother liquor salt from one basin to another. So we find in the natural salt beds numerous successions of limestone, gypsum and salt, separated by shale, clay or sand. The mother liquor salts are rarely present, and when they are, there is usually a great confusion with certain expected salts entirely absent. Many of the original salts laid down have been altered by paragenesis.

Marginal Salt Deposits—Evaporation of sea water along the margins of inland seas gives rise to extensive salt deposits. According to Grabau,[8] these may be classified as (a) marginal salt pans, (b) marine salinas, and (c) lagoonal deposits. All these have in common the characteristic that the ocean is a constant source of supply from which the salts are concentrated intermittently, sometimes to the point of complete evaporation.

The *marginal salt* pan is a shallow depression of great extent, into which the sea pours at high tide or during storms. Typical present day deposits of this type are the Rann of Cutch, India; the salt pans of the Red Sea coast of Eritrea; those of the Nile Delta; and those of the Black Sea coast. These natural salt pans have been altered by man or imitated by man for the express purpose of producing solar salt under more favorable conditions.

A *marine salina* is a salt lake near the sea, the water of which is supplied by the sea, not by overwash or canals, but by underground seepage. A good example of a present day marine salina is the Salt Lake of Larnaca, Isle of Cyprus, from which good salt has been harvested by man since the Sixteenth Century.

Lagoonal Deposits—No large salt deposits can result from the marginal salt pan or salina. If, however, a larger body of the sea becomes cut off or landlocked, as for example a lagoon or a mediterranean, a continuous or intermittent influx of sea water to replace evaporation would bring in enough salt to build up the known beds, which in some cases are thousands of feet thick. The lagoon must have a nearly continuous barrier, or bar, preventing flooding by the sea, except through one or more relatively small breeches through which sea water is supplied. Complete drying up, with the deposition of mother liquor salts, is the final fate of the lagoon.

Cut-off Arms of the Sea—During Permian time, two very famous salt deposits were laid down, one in northern Germany, and the other in southeastern

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[8] Grabau, A. W., "Principles of Salt Deposition," McGraw-Hill (1920).

New Mexico. The Permian Sea in America was really a succession of seas, extending northward from the Gulf of Mexico, through Texas, New Mexico, Oklahoma and Kansas. The Permian basin became a shallow embayment of the ocean that progressively subsided as the salts and associated sediments were deposited. As the subsidence gradually deepened southward, the centers of evaporation also shifted southward, so that the saline deposits to the south are younger than those farther north. The salt area underlies 100,000 square miles, at depths up to 2000 feet below the surface. The Permian succession of red beds, salt and anhydrite is as much as 10,900 feet thick in southeastern New Mexico. The aggregate thickness of salts is at least 4080 feet of which 1391 feet is common salt. The order of deposition was calcium carbonate, calcium sulfate, then sodium chloride, with the potash and magnesium in the mother liquors. The mother liquor salts were concentrated in a much smaller area, about 3000 square miles in extent, in southeastern New Mexico. (See Figure 2.) It is of interest that this is not in the center of the Permian Basin, but on the western rim. Thus far, the Carlsbad sylvinite beds (discovered in 1925 by V. H. McNutt) contain the largest deposit of high grade potash in the world. The potash minerals include sylvite (KCl), sylvinite ($KCl + NaCl$), polyhalite ($2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$), carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$), langbeinite, ($2MgSO_4 \cdot K_2SO_4$) together with smaller amounts of kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$), leonite ($MgSO_4 \cdot K_2SO_4 \cdot 4H_2O$) and glaserite ($(KNa)_2SO_4$).

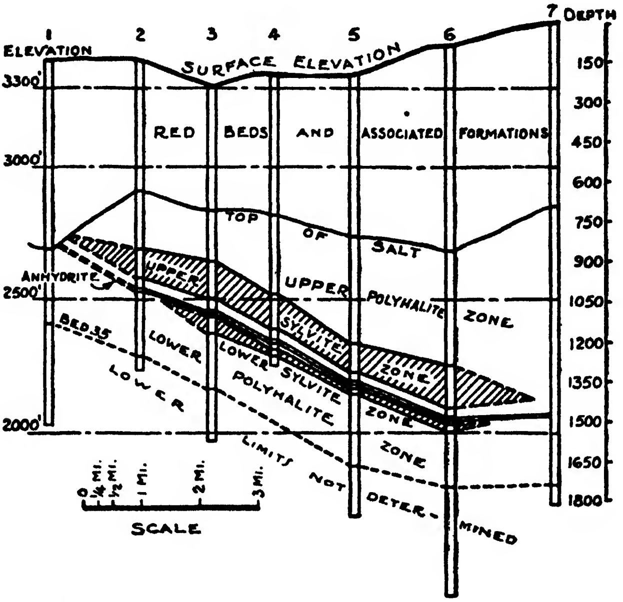

FIG. 2. Cross Section Through Sylvite Deposits East of Carlsbad, N. Mex. [Smith, H. I., Ind. Eng. Chem. *30*, p. 854 (1938)]

The German Deposits—Historically, the German deposits were discovered much earlier (at Stassfurt in 1851), but geologically they are of the same age as the Carlsbad beds. They are of the same type—namely, deposited from a cut-off arm of the sea, with all the mother liquor salts remaining. The German deposits occur in a series of sediments laid down in Permian times in the "Zechstein Sea," which covered what is now northern Germany and Holland and which extended across the present North Sea into England. The potash deposits encircle the Harz Mountains, and extend under the Hannoverian lowlands and under part of Thuringia, embracing a potential productive area of 24,000 square miles. Subsequently earth movements have greatly distorted and tilted the potash beds, producing saddles, horsts and extensive faults. The depth of the beds is quite variable, ranging from 665 to 3950 feet. The thickness is also variable, ranging from 33 to 165 feet. The estimated reserve, covering the known productive area of 580 square miles, is 72,000 million short tons of crude salts containing an average of 12.5 per cent K_2O. The potash occurs in three principal zones: the upper, or carnallite region is typically 98 to 131 feet thick; the middle, or kieserite ($MgSO_4 \cdot H_2O$) region is 65 to 131 feet thick; and the lower, or polyhalite region is 131 to 197 feet thick. At least thirty-two different salts derived from sea water are found, of which sixteen are of importance. Very little sylvinite is to be found in the German deposits.

The famous salt beds at Wieliczka in Galicia were laid down in Miocene time (later than Permian). These beds are fossiliferous but carry no potash. It is probable that this bed is of a lagoonal type. The salt deposits of Alsace are of Oligocenian age and contain a good bed of sylvinite of commercial importance.

Silurian Deposits in the United States—The Silurian salt beds of the United States are in two basins, New York-Pennsylvania-Ohio and Michigan-Ontario, separated by Lake Erie. The Silurian Sea inundated most of the central portion of North America, and these two basins, probably of a lagoonal type, became separated from the sea by a barrier of some sort. The brines were evaporated under desert conditions, though never completely. There were a number of incomplete cycles, interrupted by influx of sea and river waters. There are no mother liquor salts present—just a succession of limestone, gypsum and salt. In New York the beds dip toward the south, the top of the beds ranging from present sea level down to at least 1500 feet lower. The aggregate thickness of rock salt ranges from nothing (where the Salina outcrops in northern New York) to nearly 500 feet of salt at Watkins. At Retsof, New York, the International Salt Company mine rock salt from one of the strata, 18 feet thick and about 1100 feet below ground. This salt, in common with most rock salt, contains considerable gypsum intimately mixed with it.

A modern example of illustrating the fate of a cut-off arm of the sea is to be found in the Salton sink in southern California. It is a depressed basin at the head of the Gulf of California, separated from it by a barrier of river detritus. The floor at the deepest portion lies 273 feet below sea level, and at one time was a dry salt pan. The basin has occasionally been flooded by overflow from the Colorado River and is now occupied by the Salton Sea, a saline lake which is evaporating rapidly.

Playa Deposits. The salt playas of Nevada and California, notably Owens Lake and Searles Lake, California, owe their origin to the leaching of the decomposition products of the surrounding Tertiary sediments. The brines and the salt beds contain a high proportion of carbonate, sulfate and potash as well as appreciable percentages of borate, and thus do not resemble sea water (see Table 3).

Present day salt deposits may have been formed from older deposits, through the action of the water, wind and other agencies. Many of the sodium sulfate deposits in the Lake Lahontan region of the western United States, and in western Canada, are of this character. The origin of the alkali and sulfate, according to one theory, is as follows: most igneous rocks contain pyrite and other sulfides. The sulfides on exposure are oxidized to sulfuric acid, which decomposes the basic rocks, producing soluble sulfate. The sulfate is in part reduced to sulfide by organic matter, and the CO_2 from the atmosphere then converts the sulfide to soluble carbonates. The alkaline waters drain down into the natural basins, and in the arid conditions prevailing just east of the Coast Range and the southern Sierra Mountains, are evaporated to deposit mirabillite ($Na_2SO_4 \cdot 10H_2O$), trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$), burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) and many other salts. The mirabillite effloresces in the dry season and is scattered by the winds over a widespread area, so that during the ensuing wet season, the sodium sulfate may collect in separate basins, effectively separated from other salts.

Salt Domes—Geologically interesting and industrially important are the salt domes. These are huge vertical columns of salt based on the strata of older salt deposits, and rising toward the surface, sometimes even above the surface of the earth. They vary greatly in size but a typical dome as it occurs in the Gulf region of Texas would be Avery Island, Louisiana, which is about two miles in diameter at the surface. Its height is not known but in drilled wells the salt is still found 2700 feet down. The salt domes, according to the latest theory of Nettleton,[4] originate in a mother salt strata laid down in ancient times. Torsion balance surveys indicate the depth of this layer to be about 20,000 feet on the Gulf Coast. Below about 2000 feet, the surrounding sediments are denser than the rock salt, so that at greater depths there is a buoyant effect which tends to float the salt. Rock salt is known to be plastic, flowing slowly under pressure. The viscosity of rock salt at 18° C. is 10^{18} poises, at 80° C., 10^{17} poises. For comparison, the viscosity of asphalt at 20° C. is 10^7 poises and of shoemaker's pitch at 15° C. is 10^8 poises. Given an overburden sufficiently weak and a sufficiently long period of time, the salt would rise in columns along paths of least resistance until the supply has run out in the vicinity of the base of dome. (See Figure 3.) If the mother layer is sufficiently thick, the dome will reach surface. If not, it will remain buried, just as many salt domes are in Texas. This theory has been amply supported by dynamic models. The age of the original salt is generally referred to as Paleozoic, or from 180 to 400 million years.

Salt domes occur throughout the world. Those in Germany are of Permian origin. There are salt domes in Algeria, Hungary, and Roumania, and these constitute important sources of salt for industrial use. There is a close association of salt with petroleum bearing sands. Most oil fields produce brines along with petroleum, and in certain cases these brines have been worked up for their saline content.

Nitrate Deposits—A few natural salt deposits are rich in nitrate—notably the caliche beds in the Atacama Desert of Chile. The composition of caliche is quite variable, the soluble salts being inter-bedded with much gypsum, feldspar and clay. The soluble salts are for the most part sodium nitrate and sodium

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[4] Nettleton, L. L., Am. Soc. Petrol. Geol., *18*, p. 1175 (1934).

chloride, with smaller amounts of potassium nitrate, sodium sulfate and traces of borates, iodates and chromates. The Bolivian deposits contain much borax.

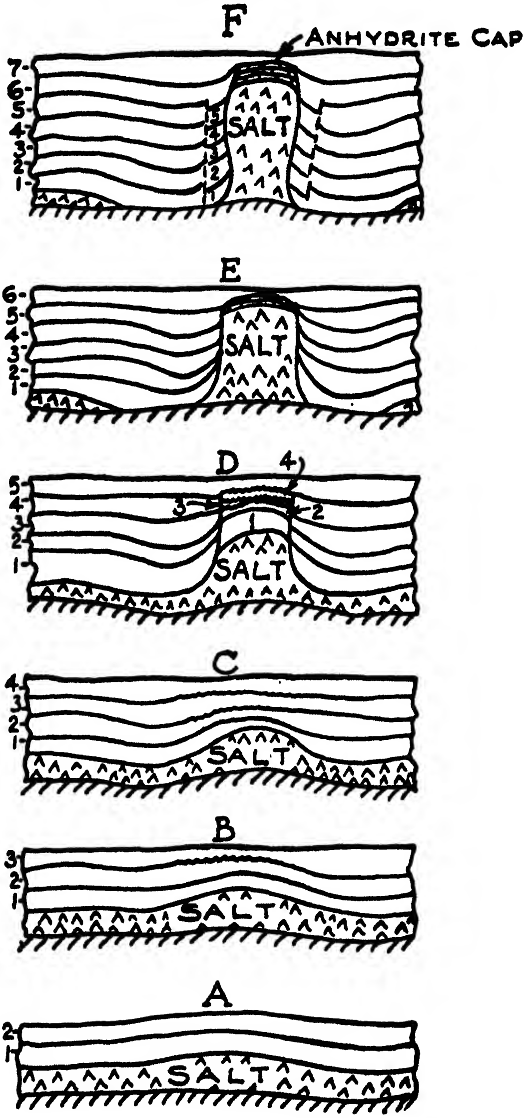

Fig. 3. Evolution of a Salt Dome (after Nettleton[4]).

The numbered layers represent successive geologic sediments. (A) Earth movement causes a slight hill. (B) The hill causes a bubble in the salt. (C) The bubble rises and draws salt from around the base. (D) Shows faulting in overburden. (E) The supply of salt is cut off. (F) Fully developed dome.

The origin of the nitrates is not fully understood although one or several of the following causes may be responsible: (a) guano from birds, possibly carried as wind blown dust to the uplands, (b) oxidation of organic matter in the soil, followed by leaching of the soil by alluvial waters, (c) fixation of atmospheric nitrogen by lightning discharges, the nitric acid being dissolved in rain water and carried over feldspathic rocks and so converted to alkaline nitrates, (d) from NH_3 in volcanic vapors and water. The presence in the caliche beds of other constituents which are common in sea water indicates a complex source for the nitrate deposits.

In conclusion, we may say that the sea is a tremendous reservoir for soluble salts of all kinds; that geologic processes have redistributed and concentrated these salts over many parts of the earth; that the older deposits constitute valuable raw materials for chemical industry and for agriculture; that the process of salt deposition is going on today as in the past; and that it is possible to control and accelerate these processes for industrial use, going directly to the sea for recovery of certain desired compounds.

TABLE 4—WORLD PRODUCTION OF SALT

For 1938 (or last year for which records are available)
Metric Tons
From Minerals Yearbook 1940, page 1430

North America, total	7,874,540
Canada	398,013
Central America	18,537
Mexico	107,701
United States	7,272,651
West Indies	77,638
South America, total	1,395,608
Argentina	264,150
Brazil	859,222
Chile (1937)	36,697
Colombia (1937)	164,636
Ecuador	13,938
Peru	34,307
Venezuela	22,658
Europe, total	15,933,451
Bulgaria	76,500
Czechoslovakia	174,000
France	1,610,276
Germany	3,280,310
Austria	94,362
Greece	102,057
Italy	1,499,075
Netherlands	164,266
Poland	642,875
Roumania	353,565
Spain (1934)	762,331
Switzerland	84,049
U. S. S. R. (1935)	4,349,500
United Kingdom	2,680,032
Yugoslavia	52,634
Other	7,619
Asia, total	6,085,809
Aden	282,510
Burma	39,319
Ceylon	36,490
China	3,000,000
Chosen	138,000
India	1,593,901
Indo-China	193,050
Japan (1937)	746,246
Netherlands Indies	74,411
Philippine Is. (1937)	48,905
Thailand	156,268
Turkey	247,293
Other	29,416
Africa, total	794,099
Algeria	74,630
Egypt	284,949
Eritrea (1936)	62,000
Ethiopia	10,000
Lybia	30,000
Angola	25,000
Sudan, Ang. Egyp.	37,532
Tanganyika	10,169
Tunisia	129,287
Union So. Africa (1937)	106,338
Other	24,164
Australia, total	128,219
Grand Total	32,211,726

COMMON SALT, SODIUM CHLORIDE

The world production of salt in 1938 was estimated at 32,211,726 metric tons (see Table 4). The world population is about 1800 million persons, so that there was produced in one year, on the average of 18 kilograms or 40 pounds of salt for every living person. As will be shown later, a very large proportion of this is used for industrial purposes. The United States, with its production of 7,272,651 tons, is the leading salt producing nation, supplying 22 per cent of the world supply.

Sources—Salt is produced from the following sources:

1. Geologically old salt deposits.
   By dry mining methods, the rock salt is brought to the surface as such.
   By wet mining methods, the rock salt is dissolved in the ground and pumped to the surface as brine.
   As a by-product from mining of other salt minerals.
2. Geologically recent salt.
   By recovery of salt from marginal sea deposits.
   By controlled solar evaporation of sea water.
   By recovery of salt from inland salt lakes, playas, frequently together with other natural salts.

The proportion of the salt produced by the various methods will vary widely in different countries according to the availability of each source, and the use to which the salt is to be put. The distribution of methods of production in the United States, in 1939, is shown in Table 5.

TABLE 5—SALT SOURCES IN UNITED STATES, 1939

Source		*Short Tons*	*Per Cent*
Rock salt, dry mined		2,035,157	21.9
Rock salt, raised as brine			
of which was evaporated	2,267,290		
of which was used as brine	4,584,177	6,851,467	73.9
Solar evaporation salt		391,287	4.2
Total		9,277,911	100.0

In Germany and France about 80 per cent of the salt produced is rock salt, whereas in Great Britain over 99 per cent of the salt is produced as brine. The production in many countries is entirely in the form of solar salt.

Manufacturing Methods—The principal salt producing states in the United States are Michigan, New York, Ohio, Louisiana, Kansas, California, Texas and West Virginia in the order mentioned, which taken together account for more than 98 per cent of the sodium chloride production. (See Figure 4.)

The processes of salt making in the United States are as follows:

1. Mining of rock salt.
   a. By dry mine methods
   b. By brine wells
2. Solar evaporation
3. Evaporation in open pans or grainers
   a. By direct heat
   b. By steam heat
4. Vacuum pan evaporation
5. Flash evaporation

Mining Rock Salt—In 1939 there were twenty-one plants mining rock salt. Practically the entire production is located in New York, Louisiana and Kansas in the order mentioned.

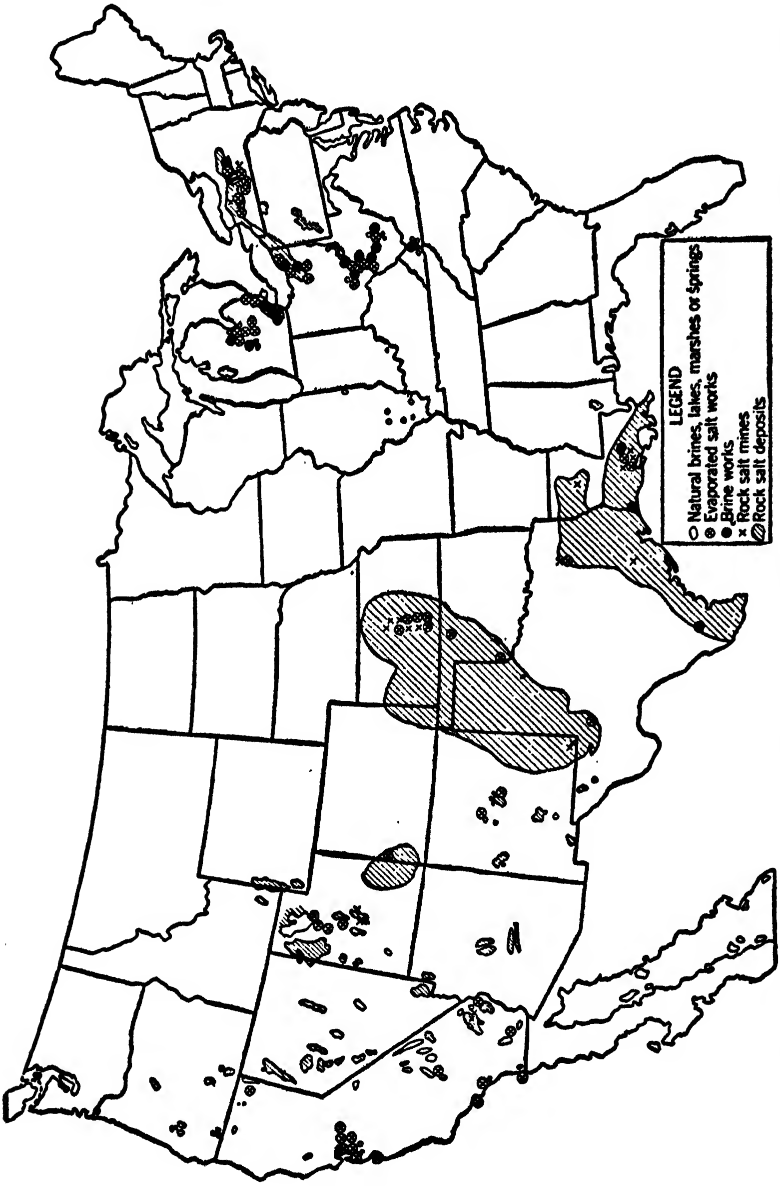

FIG. 4. Geographical Distribution of Salt-producing Plants in the United States in 1938 and Principal Known Deposits. [From Minerals Yearbook, 1939 (U. S. Bureau of Mines)]

The mining methods depend upon the thickness of the stratum which is being worked. In favorable locations, such as salt domes, the thickness of the salt is practically unlimited. In such cases the chambers and corridors within the mine are frequently more than 60 feet high. This permits the use of large and powerful mechanical shovels for loading the mined rock salt into the cars. Where the thickness of the strata is limited, as for example in the Silurian salt deposits of New York State, the chambers and corridors are only about 10 feet high. The salt is mined by undercutting and side-shearing a large block with mechanical saws. (See Figure 5.) The block is then blasted down. Electrical equipment is used to handle and transport the salt.

Skips raise the salt to the surface. The loaded skips are automatically overturned at the top of the breaker house tower. The salt is then given a primary screening and grading. Batteries of gyratory crushers are used to further reduce the salt to commercial sizes, each successive crushing being followed by a screening operation. From the hummer screens the salt flows to the packaging department and from there to cars. Bulk salt is loaded directly into box cars by means of automatic conveyers or slinging equipment.

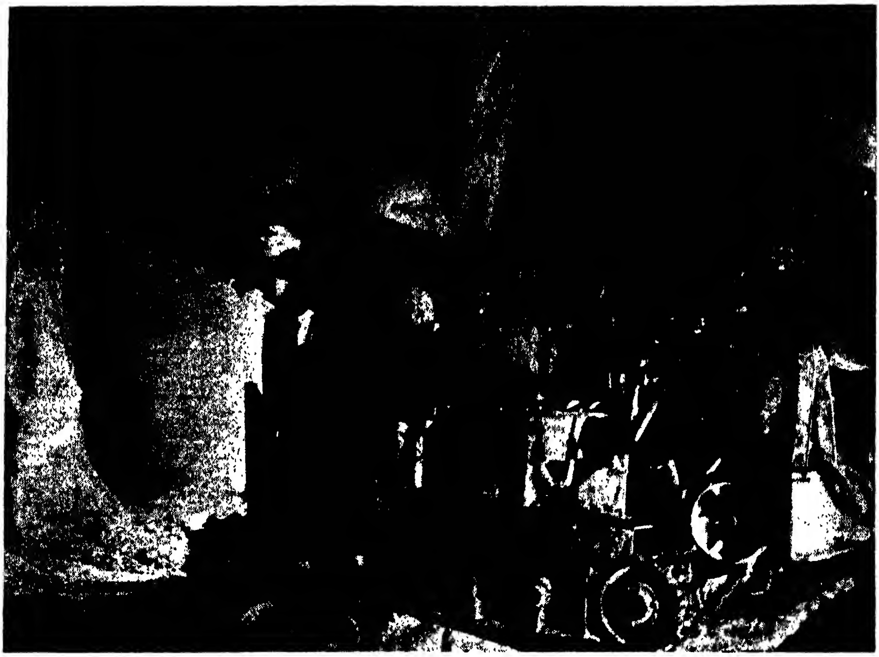

Fig. 5. Side-shearing Rock Salt in a Salt Mine. (Courtesy International Salt Co.)

Brine Wells—As pointed out on a previous page, the amount of salt raised as brine greatly exceeds the amount of rock salt mined. The requirements of the domestic alkali industry alone amount to more than 5,000,000 tons per year, which brine is used as such and is not evaporated. Likewise, most of the evaporated salt comes from brine wells.

The use of wells in removing rock salt from the solid underground deposits is really a method of mining, adapted to make full use of the solubility of the desired material. The deposits may be dry, or nearly so, hence it is necessary to pump in water to dissolve the salt. Very few wells for the recovery of sodium chloride operate on natural underground brines. On the other hand, there are deposits of natural underground brines, notably at Midland, Michigan, that are pumped and worked for valuable soluble salts other than sodium chloride.

For mining rock salt by means of wells, the method of bringing in a brine well will depend upon the thickness of the stratum being worked and also upon the purity of the salt in this stratum. A brine well sunk into a salt dome does not require the close control of the shape of the cavity as in the case when the well is sunk into a shallow stratum. The chief problems in connection with brine wells are the following:

1. The flow of the water must be such that the brine approaches saturation as it leaves the cavity.
2. Surface water and natural water from overlying strata should preferably be kept out of the cavity in order to better control the shape of the cavity.
3. The shape of the cavity should be such as to give the greatest rate of solution and production from the well.
4. As the salt dissolves there is generally left a considerable amount of insoluble mineral matter such as anhydrite sand and clay. The arrangement of the well should be such that this insoluble matter does not block the flow nor seal off the salt surface of the cavity from the action of the water.

Brine wells may be anywhere from several hundred feet to several thousand feet in depth. Two thousand feet may be considered a good average. An outer casing is generally sunk to bed rock. A somewhat smaller casing is sunk down far enough to case out all natural water. The main casing which may be from 9 to 12 inches in diameter is then sunk to the top of the salt and these three casings are sealed to the side rock with cement.[5] The arrangement of inner tubing for water and air now depends upon the method of developing the cavity.

Under Cutting Method. The water casing is lowered to within about 10 feet of the bottom of the salt stratum. (See Figure 6a.) Air is pumped down so as to maintain the brine level even with the bottom of the water casing. Fresh water is now sent down the annular space between water casing and brine tubing. The brine is forced from the bottom of the cavity up through the inner brine tubing to the surface. By manipulation of casing and tubing together with properly controlled air ceiling the salt is removed in successive layers from bottom to top as indicated by dotted lines. Debris drops to the floor and remains in the cavity. Two or more wells can be connected by shallow undercut as indicated by the solid line in the figure after which the two wells will operate as a unit, water going down one well and brine coming out the other. This method develops the cavity laterally and it is well adapted to shallow strata of salt.

Deep Air Seal Method. Where the salt is sufficiently thick and where the anhydrite sand left by the solution of the salt is particularly troublesome it is possible to develop a deep funnel shaped cavity into which all of the sand drops so that it is removed from the cavity with the brine. (See Figure 6b.) An air strata is maintained at the roof so as to broaden the funnel at the top. Solution is more rapid at the top where the water enters and saturation becomes increasingly complete as the brine drops to the bottom of the funnel.

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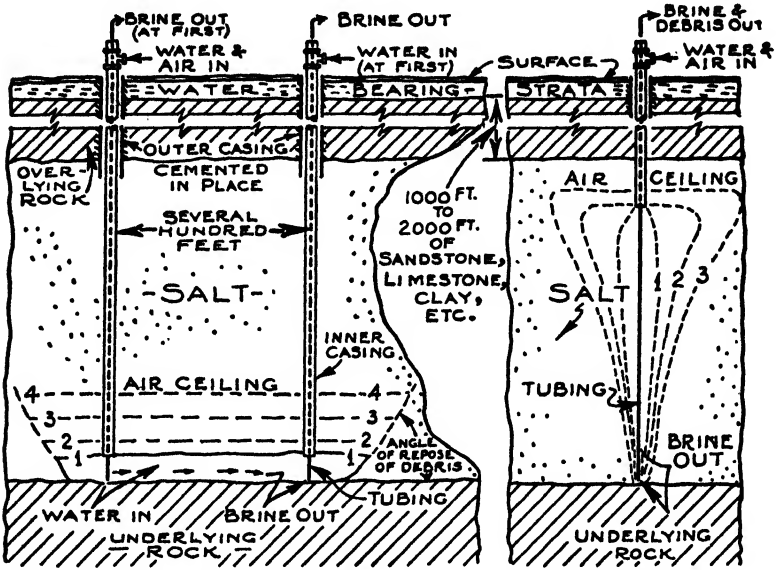
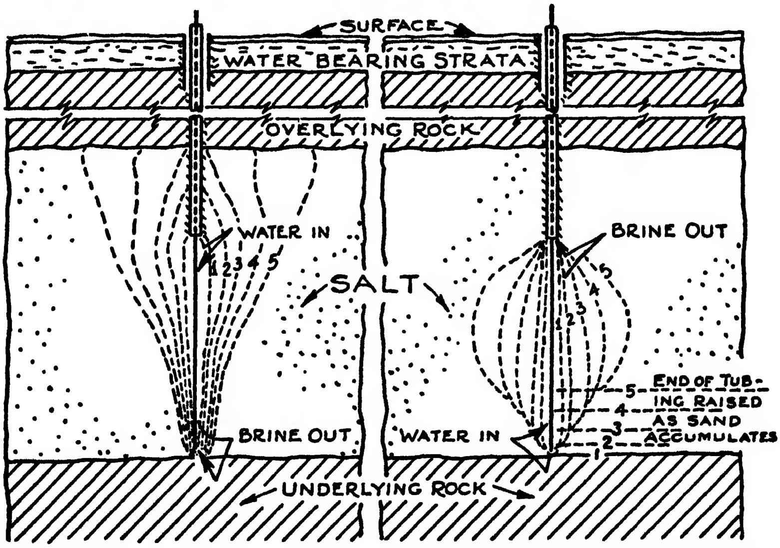
[5] For a comparison of this salt mining method with that used for sulfur, see Chapter 7.

Top Feed Method (see Figure 6c). Without an air stratum being maintained at the roof, the cavity will progressively form above as well as below the water intake. This method will eventually expose the seam between cap rock and salt. Debris falls to the apex of the cavity and is ejected with the brine. The method can be used only in deep strata of salt.



(a) UNDERCUTTING METHOD (b) AIRSEAL METHOD



(c) TOP FEED METHOD (d) BOTTOM FEED METHOD

FIG. 6. Various Methods of Operating Brine Wells.

Bottom Feed Method. Dotted lines indicate successively the extent of cavity if operation continues. (See Figure 6d.) All debris stays in the cavity and will in time cause stoppage of fresh water feed. When this occurs the tubing must be raised. An unstable condition exists within the cavity because the brine tends to remain near the bottom. It is difficult to obtain saturated brine with this type of cavity.

Raising the Brine. In the above types of well the fresh water is forced down with multiple stage high pressure pumps and the brine is forced from the well without pumping. The air pressure is maintained in the well by two stage air pumps run intermittently or continuously, as required. A well that has been properly developed and properly sealed off, will hold its air pressure for days. It generally requires several months to develop a well because the rate of solution is proportional to the surface of the cavity. The water may be forced down at the full flow (say 100 gallons per minute) in which case the brine approaches saturation gradually over a period of months. On the other hand saturated brine may be raised immediately, if the flow of water is kept low at the start and gradually increased as the cavity develops.

A somewhat less efficient method of raising the brine has been in vogue for probably seventy years. The brine was pumped by submerging a reciprocating pump below the brine level, similar to the methods used for petroleum. The piston (from 2½ to 5 inches in diameter with 3 foot stroke) was driven by sucker rods coupled together and extending to the surface. On top they were driven by one end of a walking beam of wood, the other end of beam being coupled to a crank which was driven by belt from a motor or steam engine.

Another method which requires somewhat greater horsepower than either of the above is to lift brine with compressed air. The height of water in the entry pipe is always higher than the height of brine in the exit pipe. If the end of the air line is submerged several hundred feet below the brine level (when the well is at rest), then the compressed air will emulsify with the brine or form slugs with the brine thus tending to lighten the weight of liquid in the brine pipe and raise it to the surface. It generally takes about 400 pounds pressure of air to keep the brine flowing from a well that is, for example, 2000 feet deep. Corrosion is apt to be a severe problem in this type of well.

Another more recent method of raising the brine is to use a centrifugal type deep well pump. These pumps are small in diameter and have to use about 40 stages to get the brine up. In one type of deep well pump, the electric motor as well as the pump is located at the bottom of the shaft, protected from the brine by means of oil and mercury seals.

In conclusion it may be said that where the overlying strata above the salt are air tight and water tight that the most efficient method of raising the brine is by the water pressure method together with control of the cavity by means of compressed air.

Surface Lines. At the surface the brine is generally allowed to settle and sometimes it is aerated to remove H_2S. Natural brine is generally corrosive to steel so that pipe lines are commonly built of cast iron. The surface of long underground pipe lines should be protected by wrapping with asphalt covering. Pipe lines will in the course of many years, become heavily scaled inside with gypsum.

Brine Purification—Well brines are nearly always saturated with calcium sulfate and will contain smaller amounts of calcium and magnesium chlorides. A typical brine would contain 300 to 320 grams per liter NaCl, 5 to 5.5 grams per liter $CaSO_4$, up to 0.4 per cent $CaCl_2$ and up to 0.1 per cent $MgCl_2$. It is not common practice to purify this brine for making evaporated salt, except for special uses. However, for certain industrial uses, for example, the ammonia soda process and the electrolytic alkali process,[6] it is necessary to remove calcium and magnesium. In the manufacture of metallic sodium by electrolysis of fused salt it is also good practice to remove the sulfate ion.

Removal of Ca and Mg. This is brought about by the reactions—

$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow + Na_2SO_4$$
$$CaCl_2 + Na_2CO_3 = CaCO_3\downarrow + 2NaCl$$
$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2\downarrow + CaCl_2$$

The soda ash should be theoretically equivalent to the sum of calcium and magnesium while the lime should be theoretically equivalent to the magnesium. However, because of the much greater solubility of calcium carbonate in saturated sodium chloride solution than in pure water it has been found necessary to add an excess of sodium carbonate in order to drive down the calcium concentration in the purified brine to the desired value. In ammonia soda work it is generally considered good practice to maintain an excess of about 0.8 gram Na_2CO_3 per liter. It is also considered good practice to use an excess of upwards of 0.15 gram per liter of lime to insure complete precipitation of the magnesium.[7]

In a typical brine purification plant, the soda ash is fed continuously into a high speed dissolving tank through which flows part of the brine to be treated. This solution is then mixed with the balance of the brine and is then passed through a series of slow speed reaction tanks for the purpose of completing the reaction (which takes an appreciable time), and for the purpose of improving the settling qualities of the precipitated calcium carbonate. Milk of lime ($Ca(OH)_2$) is generally added to one of these reaction tanks if magnesium is to be precipitated. This whole operation is commonly done cold in ammonia soda plants because the brine is to be used cold. On the other hand in electrolytic alkali plants it is common practice to heat the brine to be treated to 60 to 80° C. because the brine is generally fed to the cells hot. The purification will proceed more completely and more rapidly at the higher temperatures.

Care must be taken not to agitate brine violently on the way to the settlers[8] because this would break up the floc and give poor settling. The settlers may be of the shallow type, in which case a mechanism is required to remove the sludge; or they can be built with deep cones in which the sludge collects without the aid of a mechanism. The overflow from the settlers is normally crystal clear.

Removal of SO_4. The sulfate ion may be removed by the addition of barium chloride in accordance with the following reaction:

$$CaSO_4 + BaCl_2 = CaCl_2 + BaSO_4\downarrow$$

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[6] See Chapters 10 and 11.

[7] For the analogous procedure in boiler water treatment, see Chapter 6.

[8] See Chapter 2

The excess barium chloride required is very slight because of the extremely low solubility of barium sulfate. The reaction and settling equipment are conventional. The barium chloride method is expensive and is resorted to only in those cases where fairly complete removal of sulfate is required.

Removal of $CaSO_4$. Calcium sulfate as such may be removed to a considerable extent from brine by the addition of finely divided precipitated barium carbonate, according to the reaction

$$CaSO_4 + BaCO_3 = CaCO_3\downarrow + BaSO_4\downarrow$$

The reactivity of the barium carbonate is important. Plenty of time must be allowed to complete the reaction. Usually it is not possible to remove more than 90 per cent of the calcium sulfate. It has the advantage, however, that both calcium and sulfate ions are removed simultaneously; and the barium carbonate is somewhat cheaper than the barium chloride.

In the Alberger process for refining salt, part of the calcium sulfate in the brine is removed by heating the brine under pressure to a temperature of about 290° C. This process will be described more in detail in a later section.[9] It is not suitable for the preparation of purified brine although it is adapted to the production of purified solid salt.

Solar Salt—The production of rock salt and artificially evaporated salt far exceeds that of solar salt today. Nevertheless, solar evaporation is still an important industry in many districts which have a hot dry season. In California, which ranks sixth of the states in the production of salt, practically all of the salt is produced by solar evaporation. Solar evaporation is used extensively in the Philippine Islands, China, Japan, India and in many parts of Europe, notably France, Spain, Portugal and Italy, and also in South America and the West Indies. Production methods are all very much the same but vary in such details as the rate of evaporation, the length of the season and the method of harvesting. Harvesting may be crude where labor is cheap, or highly mechanized where labor is expensive.

Recovery Operations. The process now to be described is that practiced in California. The largest plants are located on San Francisco Bay in Alameda and San Mateo Counties. There are other plants at Long Beach and on San Diego Bay. The making season at San Francisco Bay covers the period April to October. From June to September inclusive there is very little rainfall and during this period the evaporation ranges from 5 to 8 inches per month. The salinity of the water in San Francisco Bay is very close to that of sea water as given on page 347. One factor which makes for success in this district is that the salt works are located on a level area of clay marl which is nearly impermeable to water and which makes an ideal bottom for the ponds. A typical salt works would cover 2000 to 3000 acres of which 75 to 125 acres are used as crystallization ponds and the remainder as concentration ponds. A plant of this size will make about 50,000 tons of salt per year. Usually only one crop is obtained per year although in extremely hot seasons, two crops.

The Evaporation Ponds. The usual method on tide water is to select a site by a solid shore line, above high tide, with a canal leading to tide water. The

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[9] See p. 371.

canal is dammed with a gate which acts as a check valve at high tide. At extreme high tide sea water is admitted to the canal, from which it is lifted by pumps to the settling ponds. Several types of pumps are in vogue, such as Archimedian screws propelled by windmills, gasoline driven centrifugal pumps and electrically driven water wheels. The settling ponds are at least 18 inches deep. There the suspended matter of the sea water settles to the bottom and preliminary evaporation takes place. The settling ponds are subdivided and in the first ponds silica, alumina, and iron sulfide precipitate. In the secondary ponds calcium carbonate precipitates. There is considerable organic growth in these ponds, including algae, diatomaceae, bacteria, insect larvae; and in the ponds containing nearly saturated brine is found the red brine shrimp, *Artemia salina,* giving the water and particularly the precipitated material a decidedly pink color.

The brine from the settling ponds next passes to a vat or "pickling pond" in which calcium sulfate precipitates as a crystalline deposit.[10] The brine is kept in the pickling ponds until it reaches a specific gravity of 1.198 to 1.209, at which point practically all of the gypsum has been deposited. As the brine approaches saturation the organic matter is killed and the solution becomes pinkish in color, a sign that brine is ready to be transferred to the crystallizing ponds.

Crystallizing ponds are usually 200 feet square, and are arranged in double rows with storage ground between. Some ponds are faced with boards. The ponds are filled to a depth of ten or more inches and when a specific gravity of 1.210 is reached salt begins to crystallize. The size of the salt crystals depends upon the temperature of the brine and rate of evaporation, in other words, on the weather. Cold weather favors small hard crystals and hot weather favors soft crystals. As evaporation continues the magnesium and calcium chloride content of the mother liquor increases. The greater portion of the salt crystallizes between the specific gravities of 1.219 and 1.234. The areas of the primary and secondary ponds are so proportioned that, on the average, there will be just enough saturated brine on hand from the pickling ponds to last out the making season. However, the weather is a variable factor. If there is an oversupply of brine the concentration is allowed to reach 1.24 specific gravity before draining off; otherwise it is allowed to increase to 1.25 specific gravity. Further evaporation would produce additional salt, but the mother liquor would be very viscous and would not drain off well. The crystallizing ponds may be filled several times each season. The brine is run in on the previous crystallizations because the salt is not harvested until the end of the season. The salt is usually harvested before the December rains begin.

Harvesting. The most modern method of harvesting is to run a power driven tractor across the salt beds. The machine is fitted with a horizontal scraper which takes up the salt and throws it on a conveyer as the tractor moves along. The salt is emptied into dump cars which run on temporary tracks laid at convenient intervals across the ponds. The mechanical lifter can turn in any direction. The salt is hauled to the plant where it is built up in piles 40 to 50 feet high. The crude salt piles are out in the weather without any roof over them. Where the piles are not disturbed there is very little loss from rain because the

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[10] See Figure 1, p. 349.

first rain forms a hard coat 2 to 3 inches thick which sheds water remarkably well. The salt is then transferred to the mill as needed where it is washed, screened and dried. The washing is done in a revolving conveyer, the crude salt being fed in one end and clear brine (from one of the pickling ponds) being fed in the other end. The salt advances countercurrently through the washer and from there it is lifted by bucket conveyer to the mill. A final washing is usually given the salt by flushing the salt in the buckets with pure fresh brine, which drains down into the salt washer.

Use of Evaporators. In recent years several of the salt plants making solar salt have put in vacuum evaporators[11] to still further purify the salt, and relieve it of a somewhat bitter taste. Most sea salt is contaminated with organic matter and iron salts; moreover, the presence of small amounts of calcium and magnesium chlorides make the sea salt somewhat hygroscropic. Sea salt made in California and purified in evaporators is generally of a very high grade, averaging 99.9 per cent pure. On the other hand sea salt from France and Spain will average about 96 per cent NaCl, the balance being chiefly $CaSO_4$, $MgCl_2$ and $CaCl_2$.

The water of Great Salt Lake, Utah, as noted in a previous section, has a much higher salinity than sea water, although the composition of the contained connate salts is quite similar to that of sea water. Considerable salt is made at Saltair, Utah, by solar evaporation methods somewhat similar to that described.

METHODS OF EVAPORATION

Open Pan Evaporated Salt—*Direct Fired Pans.* The first evaporated salt was made in iron kettles, 3 to 6 feet in diameter. The kettles were supported by their flanges at the top edge and the fire was on grates under the bottom of the kettles. The salt was lifted out to a drain board where brine drained back into the kettle.

The next apparatus used was called the open or direct fired pan. These pans were made of sheet steel and the part over the fire was usually 16 to 20 feet wide and about 115 feet long. The side walls were sloped at a flat angle and were carried 6 to 8 inches above the brine level. Drain boards were built out beyond the flaring sides and on these the salt was raked out and left to drain. The salt was then shoveled into carts and drawn by men to the storehouse where the carts were dumped from the runways to the floor. The pans were usually set about 16 feet above the floor and were set over the flues of a fire brick furnace. They were either fired with coal, wood or gas. This type of making salt is practically extinct in this country, although it is still practiced to a considerable extent abroad.

Grainer Pans. Most open pan salt today is made in "grainers" in which the heat is supplied by steam. The first grainers were made of wood and were 10 to 12 feet wide, 80 to 150 feet long and 2 feet deep. They were built without nuts or bolts, being held together with a wood frame and being keyed together on each side to hold the bottom tight. The steam was applied in 4 inch diameter pipes which extended the full length of the grainer. The pipes were connected

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[11] See p. 367.

with a header at each end and there were 4 inches between each pipe. All of the salt was raked by hand from the grainer, usually once a day. To accommodate this method there was a platform about 5 feet wide running between the grainers on which the salt was allowed to drain. The lifting of the salt from the bottom of the grainer while steam was in the pipes was a very hot and disagreeable job.

The process now to be described is that of a modern grainer system that has been widely adopted in the United States today. Grainer salt is made by surface evaporation of brine in long shallow pans. The salt is washed with brine which removes most of the impurities. The equipment is operated to produce a coarser grain than is made by any other process. The conveying and drying equipment are designed so as to reduce grain breakage.

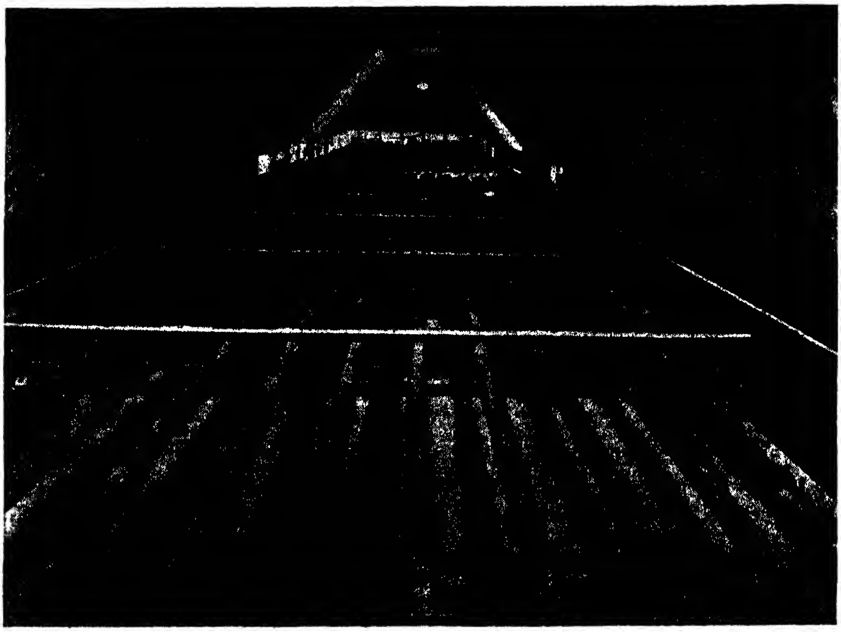

Fig. 7. An Empty Grainer Pan Showing Arrangement of Steam Pipes Used for Heating Brine for Evaporation. [Reprinted with permission of Chem. & Met. Eng. *47*, p. 565 (1940)]

Vapors pass off through openings in the hood.

The usual dimensions of a grainer are 18 feet wide by 180 feet long by 18 inches deep. The daily capacity of such a pan is 80 tons. The brine is heated with submerged steam pipes 4 inches in diameter, running the length of the pans. (See Figure 7.) A scraping conveying system along the bottom of the pans continuously advances the salt and elevates it to a drain board and eventually discharges the salt into a monel metal launder, or trough, located at one end. The mechanical scraper or rake, with about a 9 foot stroke, is operated hydraulically. The hydraulic cylinders are now made 10 inches in diameter and the water pressure required to operate them is quite low. The rakes travel about 9 feet per minute, making one double stroke in two minutes.

From the launder, the salt is elevated by a slurry pump to a crystal washer which also serves as the supply tank for the filter. The salt is usually dewatered on a top feed rotary filter, which is also supplied with hot air in order to dry the salt down to 0.10 per cent moisture. Or, the salt may be dewatered in centrifuges and dried in a rotary hot air dryer. The salt from the drier is then passed over a vibrating cooling conveyer and thence through rollers to break up lumps formed on the dryer and cooler. It is then ready for screening and packing.

The grainer feed brine will usually contain impurities of $CaCl_2$, $MgCl_2$, $CaSO_4$ totaling 0.75 per cent. Most of the chlorides accumulate in the pan brine and are eventually discharged to the sewer when the grainers are periodically cleaned. Some of the impurities adhere to the salt, but by washing the salt with feed brine they can be largely removed. Less than 10 per cent of the calcium and magnesium chlorides present in the brine appear in the finished salt. The calcium sulfate, however, precipitates with the salt in very fine crystals. Because of its fineness it can be washed from the salt, and this treatment is 75 per cent effective. The grainer pans are made of steel and, in order to prevent corrosion, the brine is kept alkaline by the addition of lime.

The crystallization of grainer salt is mostly on the brine surface where the evaporation takes place. The growth of crystals is the result of additional groups of salt becoming attached to the original nuclei. As the crystal grows, the center sinks, giving rise to the typical hopper shaped crystal or flat rectangular crystal. These crystals are supported near the surface by the surface tension of the brine until their increased weight causes them to sink.

The steam grainer system is one of the most flexible and adaptable of all salt making systems because it can operate with high pressure steam to boil the brine and produce fine grain salt, or at lower temperatures to produce, principally, flaky or hopper shaped crystals. The coarse salt made by this method is used for salting fish, hides, sauerkraut, and some kinds of meat. The flaky butter and cheese salts are made by this method, and the different grades are obtained by screening.

In the best plants using the grainer system, about one-fourth of one pound of salt is made per pound of steam condensed, although in the poorer plants the steam consumption is much higher. In some plants greater economy is obtained by running the condensed water through a second grainer, usually below the regular grainer, to take the heat out of the water. In this way coarse salt is made, which is lifted out about once a week.

Vacuum Pan System [12]—The greatest proportion of evaporated salt is made by the vacuum pan process, using 1, 2, 3 or 4 effect evaporating pans.[13] It is interesting to note that the first record we have of multiple effect evaporation is an English Patent, Number 8155, issued to John Reynolds in 1839. In the United States vacuum pans were first used about 1885. They were single units and were generally run in connection with a saw mill.

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[12] The material in this section was obtained through the courtesy of the Manistee Iron Works Company, Manistee, Michigan.

[13] See Chapter 2, p. 44, for further discussion of multiple effect evaporation.

The salt made by the vacuum process consists of small perfectly formed cubical grains, as transparent as glass. It is possible to produce extremely pure salt by this process, even from unpurified brines, simply by purging a percentage of the mother liquor as it collects, and by washing the salt.

Since saturated brine from the salt wells contains from 25 to 26 per cent NaCl, it is necessary to evaporate about 3 pounds of water for every pound of salt produced. Assuming an average steam-boiler performance of 9 pounds of water evaporated per pound of coal as fired, the fuel and steam requirements are as follows:

Number of Effects	*Pounds of Coal per Pound of Salt*	*Pounds of Steam per Pound of Salt*
1	0.45	4.00
2	0.22	2.00
3	0.15	1.33
4	0.11	1.00

The above figures are generally guaranteed by the manufacturer of the evaporator although in practice the consumptions are generally a little less. Salt is such a cheap commodity that every possible means are taken to save heat and keep the other operating costs at a minimum.

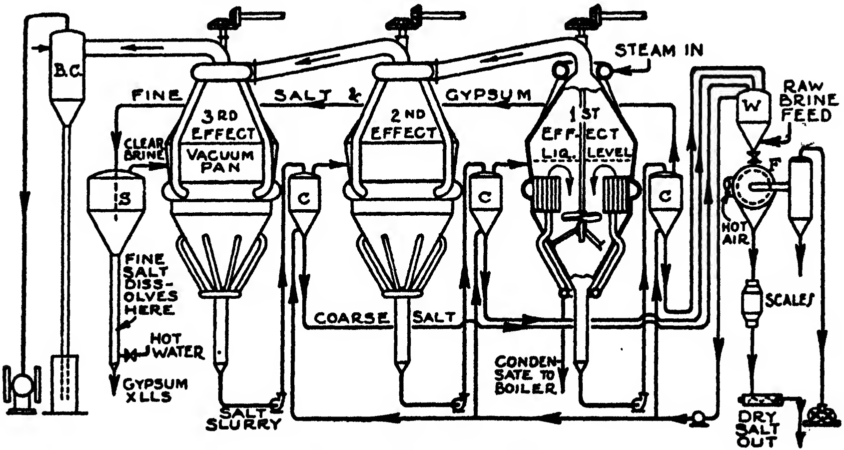

Fig. 8. Triple Effect Salt Evaporator.

In the system shown, pure salt is made from raw brine. Four effects are sometimes used: (BC) barometric condenser, (S) gypsum and fine salt settler, (C) control tank, or coarse salt settlers, (W) salt washer and filter feed tank, (F) top feed salt filter arranged for drying salt.

The Vacuum Pan. The typical salt making vacuum pan (see Figure 8) is built of cast iron which in some cases contains from 2 to 4 per cent nickel ("Niresist"). There are some steel welded pans in operation today and these are lower in first cost, although they are more subject to corrosion than the cast iron pan and are generally considered to have a shorter life. Typical pans are 18 to 20 feet in diameter and about 38 feet from top to bottom of the body. The various rings and cones are cast in segments, are accurately machined and bolted together without gaskets. The steam belt is placed in the cylindrical part. It consists of a ring shaped belt of several hundred vertical copper tubes about five feet long and two inches in diameter. A typical pan would have about 7000 to 8000 square feet of heating surface. A center well about 10 to 12 feet in diameter is left in the heating section. A large propeller suspended from the top of the body by a shaft and placed just at the bottom of the well helps to maintain circulation down through the well and up through the tubes.

The effects are fed in parallel with raw brine. Low pressure steam, generally at atmospheric pressure, but rarely at more than 10 pounds pressure, is admitted to the steam belt on the first pan. The vapor from the first pan is then conducted to the steam chest of the second pan through a distributor. Vapor from the other pans is similarly advanced until at the end the vapor from the last pan is sent to a barometric condenser. A high vacuum is maintained on the last pan. When suitable cooling water is available this vacuum is frequently within 0.3 inch (mercury) of a perfect vacuum. The use of a low temperature in all the pans helps to keep the scale from forming on the tube sheets and extending down the tubes.

Operation. Formerly the brine level was carried just above the tube sheet. Under these conditions a salt scale forms rather quickly. In about five hours the capacity of the whole apparatus is reduced to one-half and at the end of ten hours it is advisable to boil out all of the pans. This is done by emptying the brine from that particular pan quickly and refilling with water. The steam is never turned off and so the operation as a whole is not interrupted. It has been found in recent years, however, that if the brine level is carried about 30 to 32 inches above the tube sheet the trouble with salt scaling is minimized and the production can be kept at a maximum for about a week without boiling out, although after a few days of operation, unless the pan is boiled out, the purity of the salt drops somewhat.

Another difficulty that has been minimized in recent years is the formation of gypsum scale ($CaSO_4$) on the tubes. When this scale becomes 1/32 inch thick the pans must be shut down and the scale bored out of the tubes with a drill. In the earlier days the pans had to be bored out every day. It is now common practice to run many months without descaling and in some cases it is never necessary. Under the proper conditions of low temperature and high liquid level, calcium sulfate crystals are precipitated in finely divided non-adherent form along with the salt. This gypsum can be separated from the salt by differential settling.

Salt Removal. There are several methods of removing the salt from the pans. The earliest method was to leave the bottom of the leg pipe from the pan open and sealed in an open V-bottomed tank. The salt was raked out by hand. If through any accident the pans lost their vacuum the brine overflowed the seal tank and the operators had to run to higher ground. Another method which proved impractical was a rotary valve placed on the leg pipe.

Another method still in use today in some places is the bucket elevator which is arranged to remove the salt continuously from a boot placed at the bottom of the leg of the evaporator. This boot extends up alongside the pan to such a height that it will not overflow when the vacuum is relieved from the pan. The wet salt is discharged from the buckets into drainage bins, the brine running out of the false bottom back into the elevator boot. The bins, which are usually 10 feet square, hold about 50 tons of salt and are periodically spudded out, the salt being wheeled to storage bins.

Still another method in use today for removing the salt is the salt catcher which is placed on the bottom of the leg of each pan. Salt removal from the catcher is periodic.

In the latest method of taking the salt out of the different effects (see Figure 8), the salt slurry is pumped out of the bottom of the leg pipe of each pan to a separate tank *C* bolted to the side of the pan and situated on the working floor which is about 30 feet above the lower floor of the pan house. These separating, or control tanks are provided with sight glasses so that the height of the salt crystals can be seen and controlled at all times. The tanks are designed so that only the large finished crystals settle to the bottom. The small or immature crystals flow upwards and out into the same effect or on into the next effect. The gypsum crystals are carried out with the small crystals and finally reach the last pan, if the flow is straight current, or the number one pan if the flow is countercurrent. From the last control tank the fine gypsum crystals are discharged to a specially designed cone bottom settling tank *S* to be described later.

Each control tank is kept under pressure by the salt brine being pumped from the bottom of the leg of the pan by the salt pump. This pressure of ten to fifteen pounds is sufficient to discharge salt and wash brine to a small separating tank *W* over the filter wheel *F*, or the centrifugals, where the salt is finally recovered. The diameter of the control tanks and the flow of brine is regulated so that there is a constant flow of gypsum and fine salt floating away to the large settling tanks. The final washing of the salt takes place in the separating tank just above the filter or the centrifugals. If very pure salt is to be obtained it is given an additional washing on the filter, with either distilled water or steam. The fresh brine fed to the evaporating system is also used as a wash for the salt in the wash tanks above the filter and in the bottom of the control tanks.

The large settling tank, *S*, is a device for dissolving the fine salt without dissolving the gypsum. It has a 30 degree cone bottom which permits the fine crystals to slide down the sides of the cone and into a small leg pipe. The leg pipe is provided with sight glasses so that the height and density of the crystals settling down can be judged. A small stream of hot water is admitted at the bottom of the leg pipe; just sufficient to dissolve the fine salt. The gypsum crystals flow out through the bottom of the leg. The flow of the hot water is controlled so that the brine discharged with the gypsum crystals is 5 to 10° Baumé. The gypsum crystals are so fine that they will pass through a 200 mesh screen. This method of separation is not perfect but is sufficiently effective to separate most of the gypsum from the salt without any previous purification of the brine. The overflow from the gypsum separating tank is fed back into the pans. Jets of fresh brine entering into the lower cones of all pans and settling tanks keep the salt moving and prevent plugging.

In the vacuum process, the harder the plant is run the larger the crystals, whereas in the grainer process the slower rate of production the larger, denser and heavier the grain.

With the older methods of operation the salt was commonly 98 to 98.5 per cent pure. In present day operations it is possible to maintain a purity of 99.7

per cent if the pans are washed out every 36 hours or 99.5 per cent if the pans are washed out once a week.

Some plants make a practice of controlling the alkalinity of the brine in the pans, so that it is slightly alkaline to phenolphthalein. At this alkalinity a slight deposit of a basic magnesium carbonate forms on the tubes which is largely removed during the boiling out.

The salt slurry is commonly dewatered and dried on a rotary top feed filter. The drying air temperature is about 175° C. The moisture content of the salt is reduced to about 0.05 per cent. The dried salt leaving the filter is ready for screening and packing.

Flash Evaporation—*Alberger Process.* A system of flash evaporation for the production of salt has been developed to a high degree of efficiency in a plant in Michigan.[14] It is known as the Alberger process and it produces a salt with a distinctive grain and high purity. Although the process uses unpurified brine, the system is so arranged that in one part of the cycle calcium sulfate precipitates under conditions where salt cannot, and in another part of the cycle salt precipitates under conditions where calcium sulfate cannot. The plant consists of brine heaters, a calcium sulfate removal system, vapor flashers and circular grainers. The evaporation of brine is carried out in a closed circuit; that is, the brine circulates through the system continuously. All of the brine which is circulated, including about 7 per cent make-up to replace brine evaporated during the cycle, passes through the entire system of heaters, gravelers, flashers and open pans. The brine is first heated to a temperature of about 143° C. (about 35 pounds gage pressure). From the heaters the brine is passed through a cylindrical vessel filled with stones, which is called the "graveler." Since the solubility of calcium sulfate is considerably less at the elevated temperature, the brine deposits calcium sulfate on the stones. The superheated brine then passes on to the flashers where evaporation begins.

Pressure on the brine is released in steps in the three flashers in series, and each drop in pressure brings about flash evaporation and a corresponding drop in temperature. In the third flasher the pressure is dropped to atmospheric and it is here that salt begins to crystallize. The salt slurry, now at the boiling point, is passed into an open pan, circular in shape, which is provided with ploughs for raking out the salt and a hood for conducting away the vapor. In this pan, surface evaporation occurs and further salt is produced under conditions somewhat similar to the grainer system. The salt is centrifuged from the brine and the brine is recycled.

The salt produced in the third flasher is composed of microscopic cubes and needles aggregated in irregular shapes to form salt particles of high specific surface. The salt produced in the open pan is typical hopper shaped or flaky salt. The purity of the salt is said to be about 99.95 per cent and the efficiency of the calcium sulfate removal system is greater than 98 per cent.

While the use of the Alberger system cannot be justified on the basis of economy, it satisfies a special demand for high purity salt with high specific surface.

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[14] **Diamond Crystal Salt Company, St. Clair, Michigan.**

USES FOR SALT

Food Uses—Salt is largely used for culinary purposes and also in the meat packing, fish curing, dairying and other industries to prevent deterioration. Grainer salt is preferred for butter and cheese making. Number 1 grade salt with grains about ⅛ inch in size is used extensively for salting hides, making soap, salt cake, refrigerating brines and freezing mixtures. Number 2 grade, a somewhat coarser salt with grains ⅛ to ¼ inch in size, is largely sold to packers. Number 3 grade, with grains about ¼ inch in size, is used in refrigeration. Number 4, the coarsest evaporated salt, is used for stock feeding. In 1939, 152,000 tons of salt were made into pressed blocks to be used as salt licks for cattle. These blocks sometimes contain sulfur. Quick freezing of fish by refrigerated salt brine has become an important industry.

Table salt is generally conditioned with a small amount of magnesium carbonate or tricalcium phosphate to render it free flowing. Iodine is a normal component of most salt. In some localities, however, where there is an iodine deficiency, table salt is "iodized" by the addition of minute quantities (about 0.02 per cent) of potassium iodide. This is effective in the prevention of certain types of goiter which are caused by thyroid gland deficiencies which are due to lack of iodine.[15] Stock salt for cattle feeding is also frequently iodized. It has been recently found that iodized mineral feed mixtures lose 9 to 20 per cent of their iodine content during four months' storage under ordinary conditions. The iodine content can be stabilized by the addition of alkaline agents and reducing agents or by coating the potassium iodide grains with a small amount of calcium stearate.

Industrial Uses—Next to food, which is the largest market for *dry* salt, comes the chemical use. In the United States the ammonia soda industry in 1939 produced about 3,000,000 tons of alkali as soda ash which consumed about 4,500,000 tons of salt. The electrolytic caustic industry produced about 480,000 tons of NaOH, requiring 750,000 tons of salt. The salt cake furnaces consumed about 70,000 tons. These three uses[16] alone amount to 5,320,000 tons out of a total production of 9,300,000 tons.

There are literally hundreds of miscellaneous uses for salt, a few of which will now be named. It is used to put glaze on pottery and other ceramic materials. It is used extensively in "salting out" soap from saponified fats,[17] and in dye baths in the textile industry to force the dye out of the bath into the textile fiber.[18] Of late years it has been found that dirt roads can be stabilized by the addition of salt to the clay used for surfacing; such roads have a harder surface and will withstand weather and traffic much better. Salt is also used to de-ice concrete highways. It is used to regenerate the sodium zeolite used in water softening equipment[19] and for the removal of calcium and magnesium ions. A frozen eutectic mixture of salt and ice, which has been produced in cheap flake form, is used in maintaining temperatures in the neighborhood of −20° C. A small but important scientific use for salt is the production of large single crystals

[15] For a discussion of the function of iodine in this connection see Chapter 34.

[16] For further discussion of these uses see Chapter 10.

[17] See Chapter 42.

[18] See Chapter 29.

[19] See Chapter 6.

of pure halite (crystalline NaCl) for use in optical instruments. Halite optical systems pass infrared light. Salt is also used in the hydrometallurgy of sulfide ores, particularly in the production of copper, sulfur and lead.[20]

SODIUM CHLORIDE PRODUCTS

A very large and essential inorganic chemical industry is based on the use of sodium chloride as a raw material. By using a few other raw materials such as lime, ammonia and sulfuric acid, the following products are obtained by chemical methods:

Sodium carbonate
Sodium bicarbonate
Sodium hydroxide
Ammonium chloride
Calcium chloride
Sodium sulfate
Hydrochloric acid.

Of this list, sodium carbonate, sodium bicarbonate, calcium chloride and sodium sulfate are also recovered from natural deposits.

Electrolysis of aqueous solutions of sodium chloride, yields:

Chlorine
Hydrogen
Sodium hydroxide.

Electrolysis of fused sodium chloride yields:

Metallic sodium
Chlorine.

In addition, an ever-expanding chemical industry is based on the production of both inorganic and organic chlorinated compounds. These are discussed in Chapter 11.

The first five products listed under the chemical methods are made in connection with the Solvay process and are discussed elsewhere.[21] The products of the electrolysis of brine are handled in another chapter,[22] as are the products [23] of electrolysis of fused salt.

The materials manufactured by chemical methods from sodium chloride which will be discussed in this chapter are sodium sulfate and hydrochloric acid plus the recovery of such of the other listed compounds as occur in natural deposits.

SODIUM SULFATE

Sodium sulfate (Na_2SO_4) is generally known as "salt cake" for the reason that originally it was produced by the action of concentrated sulfuric acid on salt, as a first step in the production of soda ash by the LeBlanc process. Sodium

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[20] See Chapter 24.

[21] See Chapter 10.

[22] See Chapter 10.

[23] See Chapter 12.

bisulfate ($NaHSO_4$) is known as nitre cake for the reason that nitric acid was first made by treating sodium or potassium nitrate with concentrated sulfuric acid according to the reaction

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

The nitre cake was then reacted with further quantities of salt to produce salt cake. It will be noted that hydrochloric acid is an unavoidable byproduct in the manufacture of salt cake. The demand for this acid has at no time been comparable to the demand for salt cake or soda ash and this led to the abandonment of the LeBlanc process. Until quite recently the production of salt cake was paced by the outlet for hydrochloric acid. The situation today is that hydrochloric acid can be made directly from chlorine or can be obtained as a byproduct from organic chlorination reactions, without any concomitant production of salt cake.[24] On the other hand salt cake may be produced by a variety of means without the production of hydrochloric acid. For example the recent rise and growth of the kraft pulp industry [25] has stimulated production of sodium sulfate from natural salt deposits and from other byproduct operations. In addition it has even been found expedient to make sodium sulfate from sodium carbonate. This does not mean that the older salt cake furnacing operation is outmoded because there will always be situations where this is the most economical procedure. It does mean that, at least in the United States, only a portion of the demand for sodium sulfate will come from the salt cake furnace.

In 1937 the production of sodium sulfate in the United States was as follows:

Salt cake (made from salt)	189,124	tons
Natural sodium sulfate	80,053	"
Total	269,177	tons

In this same year the production of other sodium sulfate compounds was as follows:

Anhydrous pure sodium sulfate	21,797	tons
Glauber salt ($Na_2SO_4 \cdot 10H_2O$)	31,934	"
Nitre cake	36,086	"

In 1939 the production of natural sodium sulfate rose to 193,479 tons and it is probable that true salt cake production increased but slightly. The imports of crude salt cake in 1939 amounted to 1,394,484 tons, most of which came from Germany and Belgium. Because this country has produced only a small amount of its salt cake requirements in the past, the recent cutting off of imports from Europe has proved to be a tremendous stimulus to the domestic industry in the United States. It has also stimulated production of byproduct sodium sulfate from the Chilean nitrate operations.

Manufacture of Salt Cake—Salt cake is produced by the decomposition of salt and sulfuric acid. This decomposition takes place in two stages

$$\text{First: } NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$\text{Second: } NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

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[24] See Chapter 11.
[25] See Chapter 37.

Number one grade salt is usually specified and commercial 60° Baumé, 66° Baumé and 98 per cent sulfuric acid are the grades used. If nitre cake ($NaHSO_4$) is used, it usually contains 35 per cent sulfuric acid but often varies 3 to 4 per cent either way.

If pure hydrochloric acid is to be prepared the first reaction is carried out in cast iron retorts. These may be operated intermittently or continuously. They are usually 9 feet deep by 8 feet in diameter and will decompose at least six tons of salt per twenty-four hours. The pot is heated by the surrounding furnace and the bisulfate is poured at 150° C. Practically 100 per cent HCl gas may be recovered from such a retort.

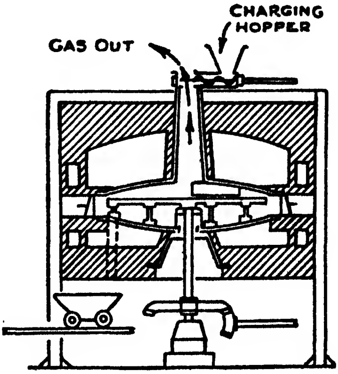

Fig. 9. The Mannheim Furnace for Manufacture of Salt Cake. [Laury, N. A., "Hydrochloric Acid and Sodium Sulfate," p. 79, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1927]

Muffle Furnace. The most important type of mechanical furnace, in which both stages or the second stage only of the decomposition may be carried out, is the Mannheim furnace. (See Figure 9.) This is a circular cast iron pan usually about 11 to 18 feet in diameter. The lower half of the pan is somewhat heavier than the upper part. Cast iron or "Duriron" scrapers keep the mass slowly stirred up while the HCl gas is distilled off through the outlet in the upper half of the muffle. The furnace is operated in a continuous manner. When it is used for both stages of the decomposition salt and acid are charged at a steady rate through the top. Salt cake is removed through a port in the bottom of the muffle. The capacity of an 11 foot pan is about 1400 pounds of salt per day. The muffle is set in a fire brick furnace and the temperature of the gas in the flue is maintained at 145° C. The draft on the muffle is regulated by analysis to 30 per cent by volume of hydrochloric acid. Starting with salt and sulfuric acid it is possible to produce as high as 60 per cent HCl in the muffle.

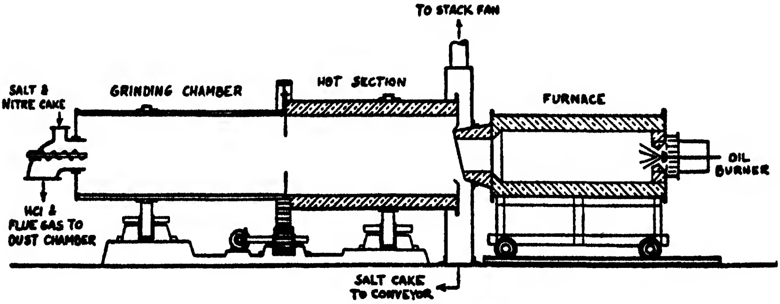

Fig. 10. The Laury Rotary Salt Cake Furnace. [Laury, N. A., "Hydrochloric Acid and Sodium Sulfate," p. 79, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1927]

Direct Fired Furnace. Salt cake is also produced in rotary furnaces of which the Laury furnace may be taken as the prototype. A plan and elevation of the furnace are shown in Figure 10. It consists of a combustion chamber with oil burning equipment and a horizontal two-chamber revolving cylinder. The rotary part is a steel shell in two sections of different diameter. The hot section has a 9 inch fire brick lining. The other section is a grinding chamber which is lined with chilled iron plates.

Salt and nitre cake are fed to the grinding chamber where they are thoroughly mixed by means of a loose rail. The HCl gas leaves the grinding chamber at about 150° C. and is then passed through a dust chamber. In the furnace proper a temperature of 537° C. is maintained. The capacity of the standard furnace, the rotary part of which is about 22 feet long and 5 feet inside diameter, is said to be one ton of salt cake per hour with a consumption of 9 to 10 gallons of fuel oil per hour. The gas from the furnace will average about 5 per cent HCl. The recovery of the HCl is discussed later in this chapter.

Production of Natural Sodium Sulfate—Sodium sulfate is found as a constituent of surface salts or lake water in nearly all the dry districts of California, New Mexico, Nevada, Oregon, Utah and Washington.[26] In Canada, there are very large deposits in Saskatchewan and British Columbia. There are also extensive deposits abroad, notably in Russia (U.S.S.R.). It occurs both in the form of lake brine and subterranean brine and in the form of Glauber salt ($Na_2SO_4 \cdot 10H_2O$) from dry lake beds. A typical lake crystal such as occurs in Saskatchewan consists chiefly of Glauber salt and would have the composition Na_2SO_4, 42-43 per cent, clay 4-6 per cent, and water 52 per cent.

Natural Crystal. One method of refining described by Pierce[27] consists in harvesting the crystals and then passing them through a roll crusher. The crystals are then washed free of mud with lake brine in a log washing machine. They are then melted in a direct-fired rotary furnace, which operation dehydrates a portion of the decahydrate leaving the balance in the form of saturated solution. The slurry is then fed to an atmospheric drum drier and the damp product scraped from the rolls is given a final drying in a direct fire rotary drier. About 71 per cent of the dehydration is accomplished in the drum drier while 29 per cent is done in the direct heat driers. The fuel consumption is said to be 450 pounds of lignite (6800 B.T.U.) and 3650 pounds of steam for each ton of anhydrous sodium sulfate produced. The purity is said to be about 95 per cent Na_2SO_4.

In Belgium, Sweden and the United States there are plants in which anhydrous sodium sulfate is recovered from a saturated solution by multiple effect evaporation in the A. S. Krystal type of evaporator, on a large scale. This type of evaporator, the sketch of which is shown in Figure 11, is well adapted to this use. The solubility of sodium sulfate decreases above the transition temperature of 32.6° C. and this fact causes rapid scaling of the heating tubes in the usual type of vacuum pan evaporator. In the Krystal device the sulfate brine is circulated rapidly through an outside heater which raises the temperature very slightly and produces a slight supersaturation. The brine is then flashed in a vacuum chamber under rather quiet conditions, which still further increases the

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[26] The origin of the sulfate deposits is dealt with on p. 349.

[27] Pierce, J. B., Chem. and Met., *44*, 718 (1937).

supersaturation. The supersaturated solution now passes upward through a bed of crystals of anhydrous sodium sulfate and here the supersaturation is broken. These crystals are maintained in a state of limited suspension and are grown large enough to stay in the crystal body and not circulate. As the crystal body grows, part of the crystals are removed periodically in a trap. In this way very pure hard round grains of anhydrous sodium sulfate are produced. This system is also used extensively on other salts.

Natural Brine. In Lynn and Terry Counties, West Texas,[28] also in Ward County, Texas,[29] there are naturally occurring oil field brines which are high in sodium sulfate. Glauber salt is produced from these brines by chilling them in a continuous tubular crystallizer. The Glauber salt is dewatered in a direct-fired rotary furnace to produce salt cake.

The evaporation of Searles Lake[30] brine results in the precipitation of the double salt, burkeite ($2Na_2SO_4 \cdot Na_2CO_3$), along with quantities of NaCl and $Na_2CO_3 \cdot 1H_2O$. These salts from the "clarifier" are first leached hot to dissolve salt. The burkeite is then leached at about 20° C. to remove soda, leaving sodium sulfate decahydrate. The filtrate is worked up for sodium carbonate and further quantities of sodium sulfate are recovered in this operation. This byproduct sodium sulfate from the potash industry is now produced on a very large scale.

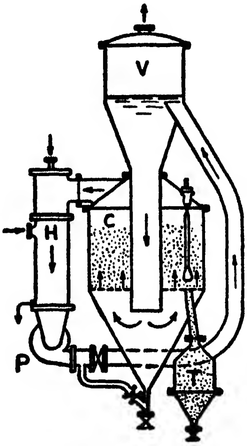

FIG. 11. A/S Krystal Type Evaporator for Sodium Sulfate. (Courtesy A/S Krystal, Hans Svanoe, Kennett Square, Pa.)

V, vaporizing chamber; C, crystallizing chamber; H, outside heater; P, circulating pump; T, trap for removal of finished crystals.

USES FOR SODIUM SULFATE

Kraft Pulp—The remarkable rise in manufacture of sulfate pulp and kraft paper[31] in recent years has established salt cake as one of the important chemicals. The bulk of the present salt cake consumption in the United States is in the South, particularly in the pulp mills of Louisiana, Arkansas, Mississippi, Alabama, Florida and Georgia, for in this region there is a vast supply of timber and pulp wood. Kraft pulp consumes from 150 to 479 pounds of salt cake per ton of pulp. Assuming 275 pounds of salt cake as a fair average consumption the total requirements of the kraft pulp industry approximated 375,000 tons in 1939. In this industry the sodium sulfate is not used as such in the cooking of the pulp.[31] The salt cake is roasted with black ash from the process, to produce sodium sulfide. The cooking liquor really consists of a mixture of caustic soda and sodium sulfide. Salt cake merely constitutes a cheap source of alkali (Na_2O) and sulfur.

It has long been known that mixtures of soda ash and sulfur are the equivalent of salt cake in the kraft process. In 1939 there was a shortage of sodium sulfate

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[28] Arizona Chemical Company, O'Donnell, Texas.
[29] Ozark Chemical Company, Monahans, Texas.
[30] American Potash and Chemical Co.
[31] See Chapter 33.

in the United States because imports from Europe were cut off. At the same time there was plenty of excess productive capacity for soda ash in the several new alkali plants in the Gulf region. Cheap soda ash and cheap sulfur, also produced in the Gulf region, therefore made it economically attractive to furnish the kraft pulp industry with a cheap mixture of these two commodities in a form known to the trade as "synthetic salt cake."[32] This product contains about 75 per cent Na_2CO_3 and 25 per cent S and is produced by sintering dense soda ash with melted sulfur until the latter has impregnated and coated the grains of the soda ash. This development demonstrates a remarkable reversal of economic conditions since the days of the LeBlanc process when soda ash was made from salt cake.

Glass—Salt cake is used in the glass industry as a small percentage of the soda ash and sand mix used in the glass furnace.[33] In this use the sodium sulfate not only contributes its share of Na_2O to the mix but the sulfur trioxide liberated acts as a stirring agent and produces a more uniform melt. For this purpose the salt cake must be very low in iron and in addition must be carefully sized so that it will not segregate from the mix. The use of salt cake in the glass industry has been diminishing. In 1937, 53,070 tons were used.

Nickel Smelting—Sodium sulfate is used in the smelting of nickel-copper matte, which operation is carried out on a large scale at Copper Cliff (Sudbury), Canada. In this process, known as the Orford process,[34] mixed copper and nickel sulfides are heated in a reverberatory furnace with sodium sulfate and some coal. The resulting melt is allowed to cool slowly and after solidifying the nickel and copper sulfide are found separated, the copper sulfide on top and the nickel sulfide on the bottom.

Another important use for sodium sulfate is in the manufacture of sodium sulfide by reduction with coal. It is probable that this use will decline because of the large amount of hydrogen sulfide now available at various petroleum refineries. The byproduct hydrogen sulfide can, of course, be absorbed in alkali to produce sodium sulfide.

Sodium sulfate is also used in the manufacture of Glauber salt and in this form it is used as a mordant in textile dyeing[35] and in medicine, especially for veterinary uses.

HYDROCHLORIC ACID

Hydrochloric acid (HCl), sometimes called muriatic acid, was first described by Valentinus in the Fifteenth Century, and extensively studied by many eminent chemists, such as Thenard, Cavendish, Priestley and Gay-Lussac. It is a gas under ordinary conditions: the liquid boils at −83° C. and freezes at −111° C. The critical temperature of the gas is 51.25° C., and the critical pressure is 81.6 atmospheres. Dissolved in water, it is the ordinary hydrochloric acid of commerce, which is generally sold in three grades: 18° Baumé, 28 per cent HCl; 20° Baumé, 32 per cent HCl; and 22° Baumé, 36 per cent HCl. A solution of 20.24 per cent in water is a constant boiling mixture which boils at 110° C. at one atmosphere.

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[32] Produced by Mathieson Alkali Works, Lake Charles, Louisiana, U. S. Patent 2,223,631.

[33] See Chapter 19.

[34] See Chapter 24.

[35] See Chapter 29.

Aqueous hydrochloric acid is extremely corrosive to most metals, and is ordinarily shipped in glass carboys or rubber lined containers. Certain metals have been developed for resisting the action of the acid, notably tantalum (which is inert) and the "Hastelloy" alloys. Very recently liquefied, anhydrous HCl has been put on the market, bottled in steel cylinders. Because of the high pressure, the containers are relatively heavy, and therefore the shipping cost makes this form of marketing prohibitive except in special cases.

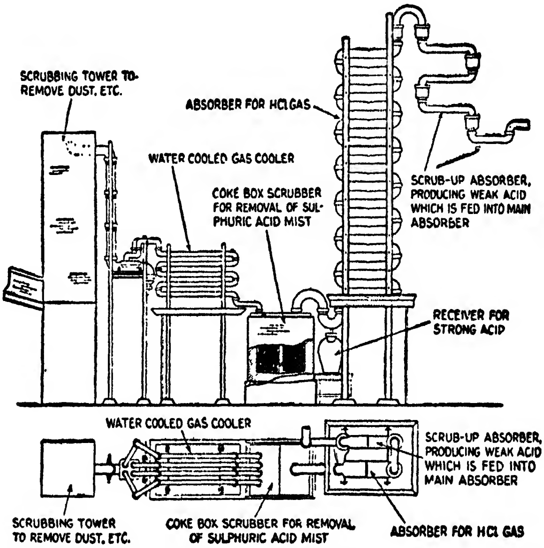

FIG. 12. Fused Silica Absorption System for Hydrochloric Acid. (Courtesy Thermal Syndicate, Ltd.)

Absorption of HCl Gas—The absorption of gaseous HCl from the salt cake furnaces is carried out in a variety of ways. An important item in the operation is that considerable heat is liberated by the absorption of HCl gas in water (650 to 850 B.T.U. per pound of HCl). The strength of the acid produced depends upon two things: the temperature of the acid and the partial pressure of HCl in the gas in contact with it. Since the absorption of HCl in water will raise the temperature, this in turn will decrease the solubility of the HCl unless the solution is cooled. Hence, all absorption devices are provided with coolers. The absorption system is more effective where cooling is simultaneous with absorption.

Concentrated HCl gas, such as is obtained from a bisulfate retort, or from byproduct chlorination reactions, or from the burning of hydrogen with chlorine, is readily absorbed in earthenware Woulff bottles, or in Cellarious tourills, which are connected in series and placed in troughs of cooling water. Another type of tourill,[36] built of fused silica, consists of a series of horizontal S-bends placed vertically one above the other and jointed with acid proof packing. (See Figure 12.) If the incoming HCl gas is hot it is first cooled down in a silica cooler, the

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[36] The "Vitreosil" absorber, Thermal Syndicate, Ltd., New York City, and the "Amersil" absorber, Amersil Co., Inc., Hillside, N. J.

sections of which are circular in cross section; they are cooled on the outside with a trickling sheet of water. The cooled gas then passes upward through the absorbing section in which it meets a stream of acid trickling downward countercurrent to it. The absorber sections are nearly rectangular in cross section, and retain a shallow pool of acid in each section. The heat of absorption is removed by trickling a sheet of water over the outside of the silica absorbers.

Recently, coolers and absorbers built of impervious graphite or carbon have been introduced. Carbon coolers are generally jacketed by steel pipes and water cooled in the conventional manner.

Stoneware plate columns, provided with a stoneware cooling coil on each plate, are now available for absorbing hydrochloric acid.[37]

Another development of considerable interest is the "Fansteel" absorber[38] (see Figure 13), which consists of a Haveg tower packed with Raschig rings. (Haveg is a phenolic plastic reinforced with asbestos fiber.) In the upper part of the tower, which is usually tapered towards the top, is placed a tantalum condenser. The heat liberated by the absorption of HCl in one part of the absorber causes evaporation of water in the lower part. This is condensed as weak acid at the top and this refluxes back down the tower. Make-up water is added at the top and concentrated acid is removed from the bottom of the absorber. The effectiveness of this compact device depends upon a very high coefficient of heat transfer on tantalum surfaces, a phenomenon not yet fully explained.

FIG. 13. The "Fansteel" Hydrochloric Acid Absorber. (Courtesy Fansteel Metallurgical Corp., No. Chicago, Ill.)

The devices just described are effective on strong HCl gas, that is to say, 50 per cent HCl or greater. With lower strength gas a scrubber of some sort is generally required on the end of any absorption system, to remove the last traces of HCl from the tail gas. Scrubbers are also effective in absorbing HCl from weak gas, for instance the 5 per cent HCl gas from the Laury furnaces. The large proportion of inert gas prevents an extreme rise of temperature of the absorbing medium. Where large quantities of weak HCl are to be absorbed it is usual to arrange several scrubbing towers in series through each of which the acid is kept circulating. Fresh water is admitted to the end tower and weak acid is advanced to the next tower, and so on until concentrated acid may be drawn out of the first tower in the series. It is also customary to cool the circulating acid on each tower in a stoneware cooling coil. The towers themselves are generally made of chemical stoneware and are filled with stoneware packing such as Raschig rings or Berl saddles.

The hydrochloric acid made in a retort is generally quite pure, but acid made from nitre cake often contains arsenic, iron, sulfuric acid, and other im-

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[37] Knight, M. A., Ind. Eng. Chem., *33*, 148 (1941).
[38] Fansteel Metallurgical Corporation, North Chicago, Illinois.

purities because of the higher temperature of roasting. The impure acid may be purified by simple distillation. This can be accomplished most readily by using tantalum heating units placed within a still of silicaware or other iron-free ceramic material, the vapors being condensed in tantalum condensers. Wherever tantalum is used in connection with hydrochloric acid care must be taken to prevent evolution of hydrogen on the metal, which would cause it to disintegrate. Such hydrogen evolution is generally the result of electrolysis. To prevent this, the tantalum is electrically insulated from all other metal parts.

HCl from the Combustion of Chlorine—In addition to the production from salt and sulfuric acid, HCl is also made by burning chlorine in hydrogen, methane or water gas and by the decomposition of $MgCl_2$ in the presence of steam.

The combustion with hydrogen may be done in a fused silica pipe; the pipe being made just large enough to enclose the flame. The chlorine is generally introduced through a nozzle or perforated pipe and the gas flame may be pointed either up or down. Reaction is quite complete without the use of any catalyst whatsoever. Air should be excluded from the burner because the heat of combustion of hydrogen with oxygen is several times that of hydrogen with chlorine; extremely high temperatures are deleterious to the silica walls of the furnace unless they be water cooled. Usually a few per cent excess hydrogen is sufficient to secure good combustion. A very pure form of HCl can be made by this method.

Hydrochloric acid may also be made by the combustion of methane and chlorine in the presence of regulated amounts of air. It is also produced in the Herschkind furnace which is essentially a water gas producer in which chlorine is admitted to the bottom of the bed of coals. The reaction here is

$$C + 2H_2O + 2Cl_2 = 4HCl + CO_2$$

Sufficient air is introduced to maintain the bed of hot coals at the reaction temperature. The HCl produced in this way would only contain about 50 to 75 per cent HCl, and moreover it is apt to contain impurities from the coke or coal used for fuel.

Chlorine was formerly made from hydrochloric acid by various means such as the Weldon process and the Deacon process. Today some chlorine is made by the electrolysis of hydrochloric acid and by oxidation with nitric acid but such processes are, generally speaking, not very profitable. A more detailed discussion of the methods and economies in making hydrochloric acid from chlorine will be discussed in a later chapter.[39]

Uses of Hydrochloric Acid—In 1937 the total production of hydrochloric acid in the United States was reported to be 121,473 tons, computed as 100 per cent HCl. Since that time, production and use have risen markedly, due to the growing demand of new uses. It is used in pickling steel for tinning; in the making of chlorides, both organic and inorganic; in the production of glue; in the preparation of fatty acids from lime soap, and for many miscellaneous purposes. A recent use which is now consuming large quantities of hydrochloric acid is the "Dowell"[40] process for activating oil wells. When a producing oil well becomes

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[39] See Chapter 11.

[40] Dow Chemical Co., Midland, Michigan.

blocked with limestone sand, or when the sand surrounding the oil well is somewhat impervious, the obstruction may be removed or the porosity may be improved by putting hydrochloric acid down the well. This acid would of course be very corrosive to the steel well casing, so corrosion inhibitors must be added to the solution.[41]

There is now a considerable use for pure anhydrous HCl gas in organic synthesis. For example, vinyl chloride, an important material for making polyvinyl plastics,[42] is made by the direct addition of HCl to acetylene:

$$HCl + CH \equiv CH \rightarrow CH_2 = CHCl$$

Rubber hydrochloride, a constituent of a new type of plastic, is made by the direct addition of liquid anhydrous HCl to rubber.[43]

RECOVERY OF OTHER NATURAL SOLUBLE SALTS

Although sodium chloride is the soluble salt which stands first in tonnage production, there are numerous other salts of the alkaline and alkaline earth metals which are of great industrial importance. Some of these salts are made by chemical methods; some can be obtained most economically from natural sources; some are obtained by both methods. In the cases where natural recovery and manufacturing processes compete, the proportion produced from each source depends largely on a constantly shifting economic balance which is fundamentally determined by demand, efficiency of manufacturing techniques, quality of natural deposits, number and kind of byproducts, disposition of the market with respect to transportation, etc.[44] Some of the manufactured products, particularly those stemming from salt, will be further discussed in a later chapter.[45] The rest of this chapter will be devoted to the discussion of important materials from the natural deposits of compounds of the alkalis and alkaline earths. In general, it may be said that the recovery of the natural materials is now on the increase and is the basis of a very vigorous and diversified industry.

NATURAL SODA

Occurrence—Natural soda occurs in many dry lake beds and playa deposits.[46] Probably the oldest historical source of soda is the Wadi-Natrum in Africa, from which the Egyptians recovered soda ash and made glass artifacts nearly three thousand years ago. The better known deposits occur in Owens and Searles Lakes, California; in Lake Magadi, East Africa; in Mexico, Persia and Southern Russia; and in Manchuria and Inner Mongolia, the Rèpublic of China. Natural soda crystals always contain considerable quantities of sodium bicarbonate (notably in combination as the sesquicarbonate, trona, ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$)) and generally also some sodium sulfate, together with smaller amounts of other impurities such as sodium chloride, calcium sulfate, and insoluble matter. In

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[41] Levey, H. H., Chem. Ind., *37*, 124 (1935).
[42] See Chapters 11 and 31.
[43] See Chapter 39.
[44] For further discussion of the effect of such an economic balance, see Chapter 1.
[45] Chapter 11.
[46] See p. 352.

a soda lake where crystals are deposited in large quantities, especially in winter time, the lower layer consists mostly of sal soda (sodium carbonate) while the upper exposed surface is the monohydrate ($Na_2CO_3 \cdot H_2O$) and the sesquicarbonate (trona). In Searles Lake there is a crystal reef of nearly pure trona, and this, at one time, was harvested as such. Typical analyses of native (unrefined) soda from various deposits are given in Table 6.

TABLE 6—ANALYSES OF NATURAL SODA DEPOSITS

Magadi Natural Soda
(To which certain treatment has been given)

	Per Cent
Na_2CO_3	94.08
$NaHCO_3$	2.31
Other soluble salts	1.89
Moisture	1.13
Insoluble	0.59

Mongolian Natural Soda
(On moisture-free basis, per cent)

	Sample No.		
	(*1*)	(*2*)	(*3*)
Na_2CO_3	76.95	51.52	69.47
$NaHCO_3$	20.62	42.75	16.65
Na_2SO_4	1.13	2.64	11.04
NaCl	1.27	2.09	0.87
Insoluble	trace	0.97	1.95

Manufacture—For many purposes, such crude natural soda is unsuited and must be refined. The cost of refining is of the same order of magnitude as the cost of manufacture by the ammonia soda process,[47] starting with salt. Only a small percentage of the total production of soda ash derives from natural sources. In the United States the total domestic output of soda ash in 1939 was of the magnitude of 3,000,000 short tons. But domestic production of natural soda ash reached about 125,000 short tons in 1939, and is still increasing. In the United States production of natural soda has been confined to Searles Lake and Owens Lake, California.

Operations at Searles Lake—One plant[48] carbonates the lake brine to precipitate crude sodium bicarbonate which is filtered, washed, and calcined to pro-

TABLE 7—ANALYSIS OF SODA ASH MADE AT TRONA, SEARLES LAKE, CALIFORNIA

	Per Cent
Na_2CO_3	99.31
$NaHCO_3$	0.84
Na_2SO_4	0.16
SiO_2	0.002
CaO	0.001
Fe	0.0003
Al_2O_3	0.01
Borate	None
H_2O	0.04

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[47] See Chapter 10.

[48] West End Chemical Company.

duce light soda ash. In another plant[49] lake brine is evaporated to recover potash,[50] and in the process of evaporation the following three salts are precipitated: NaCl, burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) and $Na_2CO_3 \cdot 1H_2O$. These salts are partially separated by hydraulic classification in the "clarifier." The salts rich in soda may be leached to dissolve soda, leaving most of the burkeite behind. Soda is recovered as the decahydrate by chilling the leach liquors. The burkeite may also be resolved into its component salts by decomposing with water at 20° C., whereby the soda is extracted, leaving sodium sulfate decahydrate. The sodium carbonate decahydrate is melted, evaporated to produce the monohydrate, and the latter salt is calcined to produce soda ash. A typical analysis of this soda ash, given in Table 7, shows that it is comparable in purity to ammonia soda process soda ash.[51]

Operations at Owens Lake—At Owens Lake, one plant[52] first concentrates the lake brine to 12-14 per cent Na_2CO_3 by solar evaporation in vats ranging from 15 to 50 acres in area. The brine is then carbonated in towers 6 feet in diameter by 80 feet in height. The CO_2 is obtained by calcining dolomite which occurs in the vicinity. This converts the soluble carbonate into the less soluble bicarbonate

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$

The sodium bicarbonate sludge is centrifuged, washed and dried, and then screened for laundry use or calcined in Herreschoff furnaces into light soda ash. Borax is recovered from the mother liquors by chilling.

Another plant at Owens Lake[53] carbonates the lake brine to produce sodium sesquicarbonate, which is calcined to a very light soda ash. This is rehydrated and recalcined to produce a denser soda ash. Still another plant,[54] recently completed, manufactures about 100 tons daily of soda ash by a new process, details of which have not been divulged. Owens Lake brine contains considerable silica, and one of the problems confronting all the plants is the removal of this silica in order to produce an acceptable grade of soda ash.

Uses for Soda—This is covered in Chapter 10.

NATURAL SODIUM NITRATE

Extraction of sodium nitrate (saltpeter) from the natural deposits in the Atacama Desert of Chile was begun in the Eighteenth Century. Exportation of natural nitrate to Europe began in 1830 but it was not until the nitrate deposits were taken over from Peru and Bolivia by Chile in 1882 that real development began. The nitrate industry grew rapidly and the revenue from the export tax became the chief source of income for the Chilean Government. English and German companies exploited the deposits which then became the chief source of nitrate and nitric acid for the whole world.

Since the advent of the Haber-Bosch process in 1912 the synthesis of ammonia from the air has become the chief source of fixed nitrogen.[55] The production of

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[49] American Potash and Chemical Corporation. See Teeple, J. W., "Industrial Development of Searles Lake Brines," Reinhold Pub. Corp. (1929).

[50] See p. 389.

[51] See Chapter 10.

[52] Pacific Alkali Co., Bartlett, Calif.

[53] Inyo Chemical Co.

[54] Natural Soda Products Co.

[55] See Chapter 8.

saltpeter in Chile reached an equivalent of nearly 500,000 metric tons of nitrogen in 1929 but declined to 71,000 tons in 1933.

Prior to 1927 the method of mining and refining the natural nitrate was rather crude and expensive. The competition from synthetic nitrogen caused the Guggenheim brothers to improve and perfect the process to a considerable degree. Since 1933 the production has been rising and in 1939 this amounted to 1,427,000 metric tons of sodium nitrate, equivalent to 238,000 tons of nitrogen. However, this only represents about 5 to 6 per cent of the total world production of fixed nitrogen. While Chile has lost its leading position in the nitrate industry, nevertheless it still remains an important source of nitrate for agricultural use.

The Nitrate Deposits—The Coastal Range in northern Chile rises abruptly from the ocean floor. Between this range and the lower slopes of the Andes lies a desert or "pampa," varying in elevation from 4000 to 7000 feet above sea level. The nitrate bearing lands lie along the western edge of this desert, along the eastern slope of the Coastal Range.[56] The beds are not continuous; they occur intermittently over an irregular belt some 400 miles long from north to south and five to forty miles wide. The sodium nitrate, along with other soluble salts, occurs for the most part as a cementing material in the outwash sands and gravels which form the eastern slopes of the Coastal Range. The harder cemented material in the deposits is overlaid with a barren overburden of loose aggregate which varies in thickness from a few inches to several feet. The high grade hard material is called "caliche" and contains over 14 per cent $NaNO_3$. The loose underburden which also contains some nitrate is called "costra." A typical analysis of a soluble salt occurring in caliche is shown in Table 8.

TABLE 8—TYPICAL ANALYSIS * OF SOLUBLE SALTS IN CALICHE

	Per Cent		*Per Cent*
Sodium nitrate	17.6	Magnesium sulfate	3.9
Potassium nitrate	1.3	Calcium sulfate	5.5
Sodium chloride	16.1	Sodium iodate	0.11
Sodium sulfate	6.5	Sodium borate	0.94
Potassium perchlorate	0.23		

* Curtis, H. A., "Fixed Nitrogen," Chemical Catalog Co., p. 52 (1932).

The sulfate generally occurs in the form of double salts although the sodium nitrate is present as a simple salt.

Mining—The improved method of mining developed by the Anglo-Chilean Consolidated Nitrate Corporation utilizes mechanical methods to strip-mine the caliche. The nitrate field to be worked is systematically sampled with a checker work of test pits at 100 meter intervals. Just ahead of the strip mining operation, however, supplemental samples are taken at 20 meter intervals. Analysis is made to show the amount of overburden to be removed as well as the thickness of the caliche to be taken. The nitrate field being exploited is laid out with semi-permanent railroad haulage lines as well as a portable electric transmission line and compressed air line. These are set up alongside the area to be stripped. The first operation consists of drilling and blasting the hard overburden which is then stripped by a drag line which backcasts the overburden on the ground already exhausted. Another drilling and blasting crew follows to break

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[56] See p. 353.

up the ore. The shovel then follows and loads the broken ore on the thirty ton ore cars for shipment to the plant. The strip worked is usually about forty feet wide and usually two to three miles in length. Upon completion of such a cut, the haulage line, transmission and air lines are moved just the width of a strip and the operation is then repeated in the reverse direction.

Refining—The modern method of refining such as is carried out at the Maria Elena plant will now be briefly described. This plant has a capacity of more than 600,000 tons of nitrate per year.

The ore is first broken in a large jaw crusher; next in gyratory crushers and lastly in cone and disc crushers. The product is ⅝ inch in size. The fine material is separated by screening. Coarse material is sent to the leaching tanks and the fine product is separately treated in a filter plant.

The first operation is the leaching out of the water soluble material. The coarse ore is leached in a series of large concrete tanks which hold about 75 tons of ore each. These are loaded from a mechanical bridge and the leached tailings are unloaded by grab buckets also operated from the bridge. When a tank is first loaded with dry ore it is filled with wash liquor from the filter plant and this liquor is circulated through the tank in circuit with a heater which derives its heat from the exhaust of the Diesel engines of the power plant. When the temperature has reached 40° C. the liquor is advanced from tank to tank until it has become nearly saturated with respect to sodium nitrate. The extraction process is countercurrent so that most of the nitrate is extracted from the ore. When this occurs, the leached ore is replaced by fresh ore and this tank is made the head end of the series. It is interesting to note that very little of the other soluble salts in the caliche dissolve because the high concentration of sodium nitrate represses their solubility.

Crystallizing is accomplished in shell and tube heat exchangers in which the warm strong liquor is pumped countercurrent to the cold depleted mother liquor. In this way the liquor is cooled to 15° C. without refrigeration. Some of the sodium nitrate has already crystallized at this temperature and this is removed by settling. In a series of ammonia refrigerated crystallizers the strong liquor is further cooled to about 5° C. at which temperature it is passed to a Dorr thickener in order to settle out the nitrate crystals. The clarified cold mother liquor is used to precool the incoming warm liquor in the head exchanger. The weak mother liquor leaves the exchanger at 35° C. and it is then pumped over an evaporating tower, after which it is used as the cooling medium in the ammonia condensers in the refrigerating plant. The weak mother liquor thus warmed is returned to the extraction unit for leaching out further quantities of sodium nitrate.

The fines from the crushing operation are extracted with the last drain-off from the leached ore and the filtrate is returned to the leaching plant cycle.

The crystallized sodium nitrate is centrifuged, after which it is briquetted and melted in a direct-fired combination reverberatory and shaft furnace. The molten nitrate is pumped to a spray nozzle which disperses the melt into droplets. These droplets solidify while falling and produce an even pellet product. The final product has a purity of 98.8 per cent $NaNO_3$. The grained product is shipped both in bags and in bulk to the three major north Chilean ports, Tocopilla, Iquique and Antofagasta.

Uses—The use of sodium nitrate for nitric acid manufacture is discussed in Chapter 8. Its use as a fertilizer is handled in Chapter 13.

POTASH AND POTASSIUM COMPOUNDS

The compounds of potassium are of outstanding importance because of their use as a plant fertilizer.[57] The development of potash production makes one of the most interesting as well as one of the most significant stories of modern chemical industry.

The 1938 production figures of the various countries of the world are given in Table 9.

TABLE 9—WORLD PRODUCTION OF POTASH MINERALS IN 1938 IN TERMS OF EQUIVALENT K_2O, METRIC TONS

From Minerals Yearbook 1940, page 1398

North and South America, total	287,532
United States	287,532
Europe, total	2,938,847
France	581,790
Germany	1,861,000
Italy	333
Poland	108.352
Spain (1935)	121,372
U. S. S. R. (1937)	266,000
Asia, total	51,059
Chosen (1937)	18,000
India	4,000
Palestine	29,059
Africa	80
Australia	53
Grand Total	3,277,571

POTASH MINING

German Deposits—The Stassfurt area in Germany supplies the greatest proportion of the world's potash today. More than 15,000,000 tons crude potash salts, averaging around 13.8 per cent K_2O, were mined by German producers in 1938. Most of this is processed to produce muriate, sulfate and the other high grade salts which the fertilizer industry now demands. The mine output was converted to more than 5,000,000 tons of salts of various grades, averaging 35.8 per cent potash, equivalent to 1,860,000 tons of K_2O.

German Mining Methods—In Germany there are at least 224 mine shafts, widely scattered, although only about 106 are actually operated, the production being controlled by the German Government. Most of the mining is done at depths of 1300 to 2000 feet, working chiefly in the carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) bed, but also in the less abundant kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$) and sylvinite ($KCl \cdot NaCl$) beds.[58] In steeply dipping deposits the potash salt is

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[57] See Chapter 13.
[58] See p. 388.

mined by overhand chamber-stoping protected by pillars, followed by back filling with waste rock salt obtained from the footwall strata. In the more nearly horizontal deposits the room and pillar method is used,[59] followed by back filling. The shafts are commonly cement lined but where water is encountered, cast iron tubing is used. The principal producing area is now the Hannover district, although the term "Stassfurt" salt is commonly applied to any German potash salt.

Refining—The crude crushed carnallite is refined by extracting the potassium chloride with a hot aqueous solution of magnesium chloride obtained from a previous operation. The concentration of this solution (about 20 per cent $MgCl_2$) is such that NaCl is not dissolved and the gypsum likewise remains behind. KCl is deposited upon cooling the solution, and this is filtered, washed and dried. Mother liquor is concentrated, giving a further yield of KCl which is less pure than the first crop. Part of the magnesium chloride is recycled for extracting further quantities of KCl and part is available for production of other magnesium compounds, including metallic magnesium.

Alsatian Deposits—The Alsatian deposits were discovered in 1904. They are about 1600 to 2800 feet below the surface and contain two beds, the upper of which contains from 6½ to 17½ feet of a good grade of sylvinite ($KCl \cdot NaCl$). The salt deposits are nearly horizontal, and are mined by the advancing longwall method. The potash is refined by extraction with a hot solution which is saturated with salt; thus the NaCl and insoluble matter is left behind while the KCl dissolves. KCl crystallizes on cooling and this is filtered off, washed and dried. The mother liquor is recycled for extracting further quantities of sylvinite. The French mines in 1938 turned out 3,374,000 tons of crude potassium salts containing 581,000 tons K_2O.

New Mexico Deposits[60]—In the United States production of potash at Carlsbad was begun in 1931 by the United States Potash Company. This was followed a few years later by the plant of the Potash Company of America and in 1940 by the plant of the Union Potash and Chemical Company. The method of mining is essentially the same in all three plants. The sylvinite bed is about 10 feet thick and about 1000 feet below the surface and this is both overlain and underlain with beds of halite (NaCl), polyhalite ($2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$). The sylvinite is really a mixture of sylvite (KCl) and salt with small amounts of carnallite, polyhalite, langbeinite ($2MgSO_4 \cdot K_2SO_4$), clay, sand and water. The K_2O content ranges from 25 to 30 per cent, on the average. The method of mining is quite similar to that described for rock salt.[61] The room and pillar method is used and the ratio of ore extracted to ore left in pillars is about 60:40. Although no effort has been made as yet to remove ore from the pillars, it is believed possible to do so because the salt overburden, which is roughly 600 feet thick, is sufficiently elastic so that instead of caving with removal of supports, it will bend until it reaches the floor. The ore is undercut, sidecut, drilled and blasted, to a depth of about 7 to 8 feet at a time. Because of the rubbery nature of the ore, with consequent close spacing of the

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[59] See p. 358.

[60] Smith, H. I., Ind. Eng. Chem., *30*, 854 (1938); McGraw, R. M., ibid., *30*, 861 (1938); Cramer, T. M., ibid., *30*, 865 (1938).

[61] See p. 357.

holes, and excessive use of powder, the cost of blasting is a large item. Broken ore is loaded with mechanical shovels or drag line loaders. Cars holding 5 tons of ore are pulled to the base of the shaft by electric locomotives and then hauled to the surface in skip elevators.

American Refining Methods—The extraction of the salts is accomplished by a variety of methods. At the United States Potash Company plant, the KCl is extracted with a hot solution saturated in respect to NaCl whereupon 90 to 95 per cent of the KCl dissolves. The solution is flash-cooled in a vacuum to deposit KCl crystals which are then filtered, washed and dried. The mother liquor is then recycled. The byproduct salt from the extraction operation is used to regenerate the zeolite water softener which supplies the plant with purified water from the Pecos River.

The Potash Company of America uses a flotation method[62] for the separation of potassium chloride from sodium chloride, the agent being lauryl amine hydrochloride. In this plant the NaCl is floated away from the KCl. In the new refinery of the Union Potash and Chemical Company the flotation agent (fish oil soap and lead nitrate) is chosen so as to float the KCl away from the NaCl. The sylvite so produced is not quite as pure as the crystallized sylvite, it having only about 58 per cent K_2O and a somewhat pinkish color. Steps are now being taken by the last mentioned potash plant to produce potassium sulfate (from langbeinite) as well as the chloride.

POTASH FROM LAKE BRINES

Searles Lake Brines—The early history of the potash production in the United States begins in 1863 when John W. Searles discovered what is now known as Searles Lake. In 1910 a strenuous search for potash began in the United States and in 1912 the Geological Survey confirmed the presence of potash in commercial quantities in Searles Lake. Searles Lake contains a solid body of crystals and except in the wet season the surface is solid enough for cars to drive on. The crystals are immersed in a brine whose composition varies somewhat at different levels. Below the 45 foot depth it has the fairly constant composition shown in Table 10.

TABLE 10—COMPOSITION OF SEARLES LAKE BRINE

	Per Cent by Weight
NaCl	16.36
Na_2CO_3	4.86
Na_2SO_4	6.85
KCl	4.74
$Na_2B_4O_7$	1.50
Others	0.07
Total solids	34.38

The first two processes tried were known as the Hornsey and Grimwood Processes but were found impracticable. An extensive investigation of the equilibrium between the salts occurring in Searles Lake brine was made under the

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[62] See Chapter 2.

leadership of the late John E. Teeple. In 1926 the American Potash and Chemical Corporation was organized and developed along the practical lines representing present practice.

The Process [63]—Brine is pumped from wells drilled in the crystal body of the lake by means of deep well pumps. This raw brine is used as the condensing medium for the potash vacuum crystallizers and for washing various filter cakes throughout the plant, before it enters the evaporators. The brine is then mixed with certain end liquors from the borax crystallizers and is then fed to a set of triple effect evaporators. These evaporators are 30 feet in diameter and 86 feet high and are provided with outside circulating heaters. The heaters are in multiple units so that they can be descaled, when they salt up, without shutting down operations. The suspended salts are removed from the liquors of each effect by continuously circulating the liquor through cone settlers called "salt traps." In these traps the salts are washed free of KCl with incoming raw brine. A final settler, known as a clarifier, separates out the salts which are rich in sodium carbonate. The concentrated liquor is now saturated with KCl and it is then flash-cooled in vacuum crystallizers to 38° C. to precipitate out potassium chloride. Enough dilution water is added to replace the water which is evaporated to cool the liquor, thus holding the sodium chloride in solution. The solid KCl is then thickened and centrifuged, washed and dried. The mother liquor is sent to the borax plant for recovery of borax.[64]

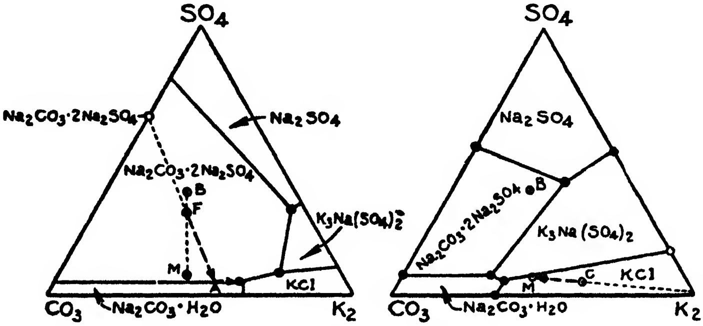

FIG. 14. Equilibrium Diagrams Showing How Potash is Crystallized from Searles Lake Brines. (After Gale)

Physical Chemistry of the Process (after Gale) [65]—Potassium chloride cannot be recovered from Searles Lake brine by isothermal evaporation at 25° C. What happens when the brine is evaporated at 100° C. can best be seen by reference to Figure 14a. Raw brine is represented by point B and plant mother liquor by point M. A mixture of these two solutions in the proportions of about three parts brine to one part of mother liquor is represented by point F. This is the mixture fed to the triple effect evaporators, operating in countercurrent fashion so that the final concentration is done at the highest temperature. During this evaporation sodium chloride and burkeite are crystallized and removed

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[63] Mumford, R. W., Ind. Eng. Chem., *30*, 872 (1938).
[64] See p. 399.
[65] Gale, W. A., Ind. Eng. Chem., *30*, 867 (1938).

continuously while the composition of the liquor travels along the line FA, the path of crystallization of burkeite, until point A is reached. At this point the mother liquor reaches saturation with $Na_2CO_3 \cdot H_2O$ which also precipitates with burkeite and sodium chloride from A to C as the liquor approaches saturation with potassium chloride in the high temperature effect. This hot concentrated liquor freed from suspended salts and containing about 19 to 20 per cent KCl, is sent to the potash crystallizing house where it is cooled for the crystallization of KCl.

Figure 14b shows the same system at 35° C. Point C representing the composition of the hot concentrated liquor, is now near the center of the KCl field so upon cooling to this temperature only KCl crystallizes out along the line CM. The mother liquor M is thus regenerated for use in the next cycle, in so far as the potash content is concerned.

The four potash plants just described account for more than 98 per cent of the production in the United States. This country is now entirely self-sufficient so far as its potash requirements are concerned and moreover it is now in a position to export potash.

Other Sources of Potash—Potash is also recovered from the flue dust from cement kilns where about 2 to 5 pounds of K_2O may be recovered for each barrel of cement made. K_2O is also recovered from the dust of iron blast furnaces where about 17 pounds of K_2O may be recovered for each ton of pig iron produced. Potash is also produced from the ash of fermented molasses, from the ash of sugar beet pulp residues, from the ash of kelp and from wool washings.

MISCELLANEOUS POTASSIUM COMPOUNDS

Potassium Hydroxide or Caustic Potash—Caustic potash is chiefly produced by the electrolysis of KCl, although it can also be produced by the causticization of potassium carbonate with milk of lime. The principal use of this alkali is soap and liquid soaps.

Potassium Carbonate—This compound is most frequently produced by the carbonation of electrolytic caustic potash. It may also be produced by the Engle-Precht process by which KCl is converted to K_2CO_3 through the addition of magnesium bicarbonate which throws down the double salt $KHCO_3 \cdot MgCO_3 \cdot 4H_2O$. Upon neutralization with $Mg(OH)_2$, the double salt decomposes. The $MgCO_3 \cdot 3H_2O$ is filtered off and recycled, while the K_2CO_3 solution is evaporated. On cooling, $K_2CO_3 \cdot \frac{1}{2}H_2O$ crystallizes, which is then calcined.

Potassium Nitrate—Known and used for hundreds of years, the nitrate is found in nature to a limited extent, but is mostly prepared from sodium nitrate by double decomposition with potassium chloride:

$$KCl + NaNO_3 = KNO_3 + NaCl$$

Solid potassium chloride is added to a hot concentrated solution of sodium nitrate. Sodium chloride first precipitates, and after its removal the solution is cooled, precipitating potassium nitrate.

Potassium Sulfate—This may be produced from KCl by base exchange in which sulfate is added in the form of sodium or magnesium sulfate. It is more commonly prepared by reaction with sulfuric acid in a salt cake furnace according to the reaction

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl$$

MAGNESIUM COMPOUNDS

The chief sources of magnesium in nature are as follows:

(a) Magnesite ($MgCO_3$), which occurs in massive rock formations in Austria, Czechoslovakia, Yugoslavia, Greece, Japan, Venezuela and, in the United States, California and Washington.

(b) Dolomite ($MgCO_3 \cdot CaCO_3$). This natural rock is widely distributed throughout the world. The proportion of Mg to Ca is not, however, always 1:1.

(c) Brucite ($MgO \cdot H_2O$). This may be considered to be native magnesium hydroxide. It is somewhat rare although there are deposits near Bryson, Quebec; Nipissing, Ontario; and Luning, Nevada.

(d) Asbestos, talc, serpentine and other minerals from which it is more difficult to extract the magnesium.

(e) Sea water and solar pond bitterns.

(f) Natural salts and natural brines. This would include such soluble salts as kieserite ($MgSO_4 \cdot H_2O$); carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$); kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$); and langbeinite ($K_2SO_4 \cdot 2MgSO_4$), such as occur in the potash beds at Stassfurt and Carlsbad. Most salt brines contain magnesium chloride or magnesium sulfate in varying degree.

Magnesium Oxide—"Caustic calcined" magnesite is obtained by burning magnesite ore in either rotary or vertical kilns, as in the making of lime. The burning temperature is somewhat lower than that for making lime. Processes closely related to this are discussed elsewhere[66] so no details will be given here. However, there are several processes for the recovery of magnesium compounds which are natural adjuncts of the industries based on soluble salts and so will be discussed.

Pure magnesia may be made from magnesite or dolomite by the *Pattinson* process. The rock is calcined, hydrated, and then treated with carbon dioxide gas or kiln gas at several atmospheres pressure. Magnesium bicarbonate goes into solution and this is filtered from the remaining calcium compounds while under pressure. On relieving the pressure and boiling, basic magnesium carbonate is precipitated. It is then filtered. This material has considerable use in the manufacture of "85% magnesia" insulation, in which it is mixed with asbestos fibre. To produce pure MgO, the basic carbonate is calcined lightly.

Magnesium oxide may also be extracted from dolomite by treatment with acid or acid salts. One method practiced commercially is to calcine dolomite, extract the CaO by reacting it with ammonium chloride (which reacts with MgO with difficulty). The $Mg(OH)_2$ is then filtered and washed free of soluble salts.

Magnesium Compounds from Sea Water—Magnesium oxide is obtained from sea water.bitterns and other brines simply by the addition of milk of lime which precipitates the magnesia according to the reaction:

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2\downarrow + CaCl_2$$

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[66] See Chapter 22.

The solubility of $Ca(OH)_2$ is about 1.8 gms. per liter at 20° C. while the solubility of $Mg(OH)_2$ is only 0.009 gm. per liter. In extracting pure magnesia from sea water a large plant[67] on the Pacific Coast pretreats sea water with a small amount of lime to remove the bicarbonate hardness.[68] The sea water is settled and clarified by filtration. The milk of lime next used is prepared from purified fresh water and it is mechanically classified to reject sand and other impurities. The lime added is made equivalent to the magnesium content of the sea water and, after reaction, the slurry is thickened in a large concrete settler. The thickener underflow is then washed free of any adhering sea water in special towers designed for the purpose, in which the magnesia retains its flocculent consistency. The magnesia slurry is then carbonated, boiled to remove excess CO_2, and filtered. The magnesium carbonate is then calcined to produce either light or dead burned MgO.

Starting with sea water, the calcium sulfate is not precipitated during the recovery operation just described. Starting with sea water bitterns,[69] however, a special step is required for precipitating the high sulfate content of the bittern as $CaSO_4$ by the addition of $CaCl_2$.

$$MgSO_4 + CaCl_2 = MgCl_2 + CaSO_4\downarrow$$

After that it is permissible to add the milk of lime without danger of contaminating the magnesia with $CaSO_4$. The calcium chloride brine is recycled. The useful products from these sea water bitterns include refractories, magnesia insulation, milk of magnesia, magnesium carbonate. Magnesia products find use as pigments in foods, dental formulas, medicine, oil refining and in the treatment of acid soils in agriculture.

Magnesium Chloride—Many natural brines, such as occur in oil wells, contain magnesium chloride. Where there are no sulfates present the $MgCl_2$ may be removed by a simple evaporation of the brine. Because they are less soluble, other salts such as NaCl and KCl are thrown out during the evaporation. The magnesium chloride is usually obtained as the hexahydrate. Some brines, notably those in Michigan,[70] contain considerable calcium chloride so that it is necessary to separate these two very soluble salts. This is done by crystallization methods by which the magnesium chloride is first separated out as tachhydrite ($CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$). This double salt may be decomposed with water, after which the magnesium chloride may be crystallized as the hexahydrate. Still another way in which magnesium chloride may be separated from calcium chloride is by means of the reaction

$$MgO + CaCl_2 + CO_2 = MgCl_2 + CaCO_3$$

Magnesium chloride may be also extracted from naturally occurring potash salts. For example the mineral carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) may be treated with just sufficient hot water to dissolve the magnesium chloride, leaving most

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[67] Marine Magnesium Chemicals Corporation, South San Francisco, California; Chesny, H. H., Ind. Eng. Chem., *28*, 383 (1936); Manning, P. D. V., Chem. Met. Eng., *43*, 116 (1936).

[68] For the details of this treatment for hardness, see Chapter 6.

[69] Westvaco Chlorine Products Corporation, Newark, California; Manning, P. D. V., Chem. Met. Eng., *45*, 478 (1938).

[70] Dow Chemical Company, Midland, Michigan.

of the KCl, NaCl and other impurities in the solid phase. In Carlsbad, New Mexico, potassium sulfate is recovered from the mineral langbeinite by means of the reaction:

$$K_2SO_4 \cdot 2MgSO_4 + 2K_2Cl_2 = 3K_2SO_4 + 2MgCl_2$$

The mother liquors are thus rich in magnesium chloride.

Magnesium chloride is used extensively in the manufacture of oxychloride cements. These cements are very hard and flexible and consist of a mixture of magnesium chloride, magnesium oxide, sawdust and other filling materials. It has been found, recently, that the addition of copper powder greatly improves the strength and wearing qualities of these cements. Magnesium chloride is also used as a refrigerating brine because of its very low eutectic temperature.

Magnesium chloride is also the best raw material from which to make metallic magnesium.[71] For this purpose it is usually dehydrated. The hexahydrate may be dried down to the dihydrate with very little decomposition. If, however, the dihydrate is further dried by conventional methods it dissociates to form magnesium oxychloride. To prevent this the dihydrate can be dehydrated in an atmosphere of dry HCl gas. Although this process was practiced by the Dow Chemical Company, at Midland, Michigan, for many years it now appears that one of the lower hydrates of magnesium chloride can be added directly to the fused electrolytic bath. In a new plant of the Dow Chemical Company at Freeport, Texas, MgO is recovered from 100 million pounds of sea water per day.[72] The MgO is then dissolved in hydrochloric acid, which is derived from the anodic gas from the electrolytic magnesium cells, to produce a solution of magnesium chloride. This solution is evaporated to produce a lower hydrate in powder form. After briquetting, this material is fed to the anode compartment of the cells in the production of metallic magnesium.

In Germany (I. G. Farbenindustrie) and in England (Magnesium Elektron Ltd.), calcined magnesite is mixed with coke and chlorinated in a shaft furnace at about 1000° C., to produce fused anhydrous magnesium chloride, according to the reaction

$$MgO + C + Cl_2 = MgCl_2 + CO$$

After filtering the molten salt through carbon to remove solid particles it is then flaked and ready to use in the electrolytic bath. Most of the chlorine required for the chlorination is obtained from the electrolysis of the magnesium chloride.

Magnesium Sulfate—Epsom salt ($MgSO_4 \cdot 7H_2O$) is found in many mineral springs. The most important natural source is kieserite ($MgSO_4 \cdot H_2O$). The latter salt is difficultly soluble in water but on long standing in contact with water it is converted to Epsom salt. Magnesium sulfate may be also obtained from the mineral kainite ($MgSO_4 \cdot K_2SO_4 \cdot MgCl_2 \cdot 6H_2O$), or by the action of sulfuric acid on MgO, $MgCO_3$ or dolomite. It may be also obtained by reacting burned dolomite with gypsum in the presence of CO_2. This salt is used extensively as a medicine. It is also used in the finishing of cotton fabrics and for weighting silk, paper and leather, and for textile dyeing.

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[71] For a description of the making of metallic magnesium, see Chapter 24.
[72] For the magnesium content of sea water, see Table 2.

BROMINE

Bromine, the second of the halogens in abundance and importance, is a liquid which boils at 63° C. In the form of bromides it occurs to the extent of about 0.064 gram per liter, or approximately ½ pound per 1000 gallons, in sea water. Bitterns from sea water evaporation as they occur in the San Francisco Bay District will contain 1.5 to 2.0 grams per liter of bromine. There are many natural brines containing from 0.1 to 1 gram per liter of bromine. If the concentration is about 0.3 gram per liter or over it is practical to recover the bromine as a liquid in one step by the direct chlorination of the brine.

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2\uparrow$$

In the Kubierschky system the brine is preheated to the boiling point and flows down a stoneware tower of special design containing a number of compartments. The chlorine enters the bottom compartment and works upward. In each compartment, however, the movement of the vapors is vertically downward in order to get better distribution of the heavy halogen containing vapor with the brine. The vapor leaving the top of the tower contains bromine, steam, and a small amount of chlorine. After condensation the two liquid layers are separated and the bromine water (the upper layer) is returned to the tower. The chlorine is removed from the bromine by distillation. The chlorine consumption will depend upon the bromine concentration: at 0.3 grams per liter about 1.3 pounds of chlorine per pound of bromine are required; and at 4 grams per liter about 0.57 pounds chlorine per pound of bromine are required. The recovery of bromine is said to be 80 to 95 per cent respectively.

Bromine from Sea Water—A different procedure is required for recovery of bromine from sea water. The Ethyl-Dow process as carried out at Kure Beach, Wilmington, North Carolina, will now be briefly described.[73] The sea water intake is located where full strength sea water is always obtainable. The waste water effluent is discharged into a river where natural currents remove it from the area around the sea water intake. The sea water is settled, screened and pumped to storage. From there it is pumped to the top of the blowing-out towers. (See Figure 15.) On the way up it is treated with a 10 per cent sulfuric acid solution to lower the pH to 3.5 and repress the hydrolysis of the chlorine. Gaseous chlorine is metered into the flowing stream. Air in large volume is blown in at the bottom of the towers in order to strip out substantially all of the bromine. The bromine-containing air is next passed laterally through a series of bromine absorption towers through which the air is contacted with a circulating solution of soda ash. The reaction here is

$$3Na_2CO_3 + 3Br_2 = 5NaBr + NaBrO_3 + 3CO_2$$

The stripped air is removed by the exhaust fans which pull the air through the entire system. The alkaline solution is advanced from tower to tower until it becomes completely brominated. The bromate solution is then acidified with sulfuric acid and steam distilled in a tower from which bromine is evolved. Bromine is a difficult liquid to handle, so it is almost universal practice to react it

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[73] Stewart, L. C., Ind. Eng. Chem., *26*, 361 (1936).

with ethylene to produce ethylene dibromide. The ethylene may be produced either by dehydration of ethyl alcohol over a catalyst or it may be obtained from olefinic gas from a petroleum refinery. The ethylene dibromide is generally purified by distillation.

In 1938, the plant at Wilmington, North Carolina, produced 1,343,000 gallons of ethylene dibromide, making it the largest single producer in the world. At a new plant at Freeport, Texas, the production will probably be much greater. Bromine is produced from salt well brines by five companies in Michigan and five in the West Virginia-Ohio area. Bromine is also produced from sea water bitterns in California and from brines from Searles Lake. Some concentrated products of this latter brine carry one hundred times as much bromine as sea water. Bromine is also recovered from the Dead Sea in Palestine and from sea water bitterns in Italy and Japan.

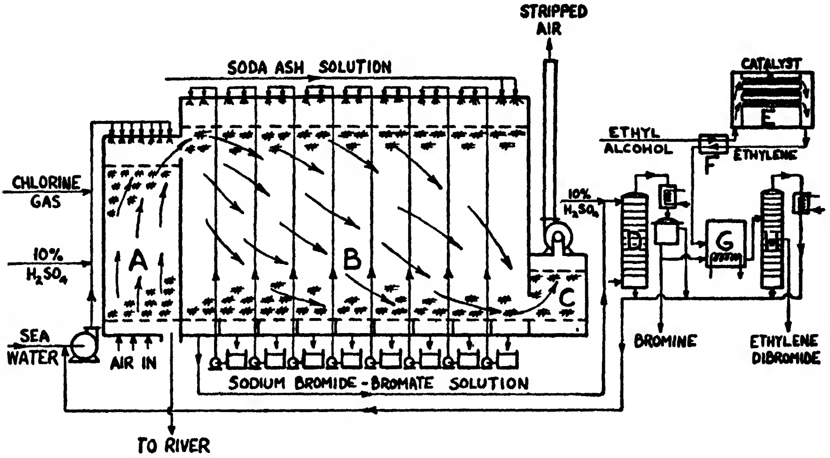

Fig. 15. Diagram of Bromine Extraction Unit. [Stewart, L. C., Ind. Eng. Chem. *26*, p. 361 (1936)]

Uses—Ethylene dibromide is mixed with tetraethyl lead in making compounds for anti-knock motor fuel. The demand for high octane gasoline steadily increases and the production of bromine for this purpose has increased in spectacular fashion. The production in 1940 was about 50,000,000 pounds of bromine. Bromine is also used in metallurgy (bromo-cyanogen process), in the manufacture of bromides for pharmaceutical and photographic purposes and in the manufacture of disinfectants.

IODINE

Iodine is a constituent of sea water and may be recovered from concentrated sea water bitterns or from the ashes of seaweed (kelp). It also occurs in oil field brines and in the mother liquor from the Chilean nitrate recovery operations. Chile has been the most important producing area for years although substantial quantities have been produced in France, the United Kingdom, Netherlands Indies, the United States and British Indies. The leading producer in the United States is the Dow Chemical Company operating on sea water brines at Long

Beach, California. The total production in the United States in 1937 was about 300,000 pounds and the iodine imported to the United States that same year was nearly 2,000,000 pounds. In recent years domestic production has increased and imports have decreased.

Iodine from Kelp—Various types of seaweed (*genus laminaria, genus fucus*) are collected at ebb tide, dried in much the same manner that hay is dried and then burned in long, low kilns of rock. After several burnings, a floor of ash, 15 to 20 inches thick, is built up. The ash content of the weed is generally about 5 per cent and the iodine content of the ash will vary from 0.2 to 2 per cent. The ash of the kelp is lixiviated in vats with hot water and then the solution is run off at a gravity of 1.2 to 1.23. The solution is evaporated in open boiling pans and the potassium salts are crystallized out.

In the modern French process, the kelp liquor is neutralized with sulfuric acid which releases CO_2, H_2S and S. When the solution has been freed of these substances it is treated with copper sulfate. This precipitates the iodine from the solution as cuprous iodide which is filtered off and washed with water. Iodine is separated from the cuprous iodide by heating it with manganese dioxide, the iodine subliming off.

Potassium iodide is prepared from the cuprous iodide, by heating with an excess of potassium carbonate at 450° C. according to the reaction:

$$2CuI + K_2CO_3 = 2KI + CO_2 + Cu_2O$$

The excess of potassium carbonate is neutralized with sulfuric acid and the potassium iodide is separated from the potassium sulfate by fractional crystallization.

Iodine from Caliche—In the Chilean process, the mother liquor from the nitrate plant contains about 8 grams per liter of iodine and 70 per cent of this is recovered. The first processing material used is soda ash. Since soda ash is not a readily obtainable commodity in the uplands of Chile, it is prepared in crude form by furnacing sodium nitrate with coal. The soda ash is leached and then treated with sulfur dioxide flue gas from a sulfur burner. The sodium bisulfite liquor is added to the iodine-containing mother liquor, and this causes precipitation of the iodine according to the following reaction:

$$2NaIO_3 + 5NaHSO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2\downarrow$$

The supernatant liquor is returned to the caliche processing plant. The iodine sludge is washed, filtered and pressed into cakes. The cakes are then placed in a cement lined retort which is fired with coal. The iodine sublimes and is condensed in an air-cooled, ceramic condenser. This condenser is taken down at intervals and the iodine is scraped from the sections and packed into 55 kilogram kegs.

Iodine from Brines—Iodine is recovered from oil field brines by either the activated carbon process or the silver nitrate process. In the *carbon process* the brine is treated with sodium nitrite and sulfuric acid, which liberates iodine.

$$NaNO_2 + H_2SO_4 + NaI \rightarrow Na_2SO_4 + \tfrac{1}{2}I_2 + NO + H_2O$$

The iodine concentration being very low, the solution is then agitated with activated carbon which adsorbs the free iodine. The carbon is filtered off and then leached with alkali, the iodine being converted to sodium iodate. This solution is next concentrated by evaporation and then chlorinated in a pot still. The iodine sublimes out of the liquor and is condensed in a ceramic condenser. It is then crushed, washed and air dried, taking care that the iodine in the air from the drier is recovered by scrubbing.

In the *silver nitrate process*, the brine is treated with silver nitrate to precipitate silver iodide. This is contacted with steel scrap which precipitates metallic silver and leaves ferrous iodide in solution. The solution is treated with nitric acid to recover the silver nitrate and then chlorine is added to liberate the iodine as in the method just previously described. The crude iodine is dried over concentrated sulfuric acid and then crushed, washed and dried.

Uses—Iodine and iodine compounds have very valuable therapeutic properties. Iodine is used in the aniline dye industry, in the manufacture of iodoform and in the production of pure potassium iodide which is extensively used in medicine and photography.

CALCIUM CHLORIDE

This salt is contained in sea water and in many natural brines and bitterns. In 1939 the production from natural brines amounted to 108,000 tons. It is obtained as a by-product from the recovery of magnesium chloride in Michigan brines. For refrigeration, a mixed calcium-magnesium chloride (basis 75 per cent $CaCl_2$) is also produced on a considerable scale.

Probably the simplest process for recovery of calcium chloride is from the distiller waste liquor of the ammonia soda process. This is described in Chapter 10.

Uses—Calcium chloride is used extensively in the refrigeration industry as a brine because of its very low freezing point (−55° C. for 30 per cent $CaCl_2$). It is also used in laying the dust on dirt roads in rural communities, notably in New England and in Canada. It has also been successfully used in stabilizing dirt roads by incorporating it in the clay used in the surfacing. In the form of a solution, it is used for dedusting coal and coke. Of the total consumption, it has been estimated that 39 per cent is used for road treatment, 15 per cent for coal treatment, 12 per cent for ice control (for example, on roads) and 6 per cent for refrigerating brines. This leaves 28 per cent for miscellaneous outlets.

BORON COMPOUNDS

World reserves of boron minerals are abundant, but known sources are confined to a few countries; chiefly the United States, Chile, Argentina, Peru, Italy and Turkey. It has also been reported in Tibet, Persia, India and Ceylon. Perhaps the most interesting operations are in Italy where sassolite, or natural boric acid, is a joint product of the utilization of volcanic gases which also yield ammonia, carbon dioxide and heat and power from natural steam. The principal natural borates of commercial importance are as follows:

Mineral	*Approximate Composition*	*Principal Deposits*
Tincal (natural borax)	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	United States, Tibet
Kernite (rasorite)	$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$	United States
Colemanite	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$	United States
Ulexite (boronatrocalcite)	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$	United States, Chile, Argentina, Bolivia, Peru
Priceite (pandermite)	$5CaO \cdot 6B_2O_3 \cdot 9H_2O$	Turkey (Asia Minor)

Manufacture—Up until 1928 most of the borax was produced from colemanite, by decomposing it with a solution of sodium carbonate and bicarbonate. The $CaCO_3$ was filtered off, the filtrate was concentrated, and the borax was crystallized out by chilling.

From Kernite—A much more important source at present is the mineral kernite, which is mined in Kern County, California. The crude ore contains about 29 per cent B_2O_3, mixed with considerable clay and shale. It is crushed, calcined, concentrated to remove the clay and shale, the concentrate running about 45 per cent B_2O_3. At the refinery,[74] located at Wilmington, California, the crude is converted to borax by dissolution under pressure in hot water. The solution is filtered, and chilled to crystallize pure borax.

From Searles Lake Brine—Borax is now produced in large quantities (about 100,000 tons per year) as a byproduct from the potash recovery operations at Searles Lake.[75] The mother liquor from the potash plant at 38° C. is pumped to crude borax vacuum crystallizers where it is cooled to 24° C. The cooling medium is liquid ammonia which is expanded in helical coils in the head end of the crystallizer. The water condensed is refluxed to the boiling liquid to avoid concentration of the solution and consequent precipitation of potassium chloride with the crude borax. The crude liquor containing borax in suspension is sent to the thickener, the thickener underflow is filtered, and the cake from the crude borax filters is refined to produce commercial borax. Boric acid is made by reaction with sulfuric acid.

Uses of Borax—Although borax was used as a flux in fire refining of gold as early as the Fourteenth Century, large tonnage was not employed until the new discoveries in California reduced the price of borax to about $30.00 per ton in 1920. The average price in 1939 was about $23.50 per ton at the producers' plants. Borax is now used extensively in glass manufacture, particularly in making the high melting boro-silicate glasses (as for instance "Pyrex" glassware which contains from 12 to 14 per cent B_2O_3). It is also used in enamel making, the mix containing from 29 to 40 per cent of borax. It is used in the manufacture of soap and detergents; as a preservative in pastes and glues; and for disinfecting citrus fruits. Recently boron has been found to be one of the minor elements that stimulate plant growth and inhibit certain plant diseases. Borax already is included in many mixed fertilizers. Boron carbide, a recent discovery, is the hardest artificial abrasive known.

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[74] Pacific Coast Borax Co.

[75] American Potash & Chemical Corporation. Borax is also made at Searles Lake by the West End Chemical Co. and at Owens Lake by the Pacific Alkali Co. See p. 390.

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CHAPTER 10

ALKALI AND CHLORINE PRODUCTION

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INTRODUCTION

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The manufacture of alkali[1] is one of the basic operations of the chemical industry. It is one of the keys to modern civilization because alkali products are essential for the manufacture of most of the goods which civilized people use for clothing, food, shelter, transportation and general living. Alkali is essential in the manufacture of nitrate fertilizers, glass, soap, paper and textiles; and chlorine (by-product of the alkali industry) is essential in water purification, the manufacture of paper pulp, high test gasoline, chlorinated solvents and dyes. The complete list of uses for alkali and chlorine would be a very long one indeed and one may conclude that the rise of the alkali industry not only coincides with but is to a large extent responsible for, the chemical age in which we now live.

The raw materials for the alkali industry are few in number, widely distributed, and available to practically any country, small or large, which may wish to start on the road toward economic self-sufficiency. These raw materials are salt, limestone, fuel, water and air. The distribution of alkali plants throughout the world is given in Table 1.

The distribution of alkali plants in the United States is given in Table 2, and of chlorine plants, in Table 3.

The two main divisions of the alkali industry are: the ammonia soda process, also known as the Solvay Process after its inventor, and the electrolytic process. The overall reaction of the ammonia soda processes may be written

$$2NaCl + CaCO_3 = Na_2CO_3 + CaCl_2$$

although taken by itself this reaction proceeds in the reverse direction. The main product of this process is thus seen to be sodium carbonate or soda ash. Its second principal product is caustic soda, produced by a second reaction:

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$$

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[1] "Alkali" is not a word with a precise definition but it commonly refers to the hydroxides or carbonates of sodium or the other alkali metals.

The principal products of the electrolytic process are caustic soda and chlorine. In a more general way this process may be represented by the equation, Salt + Power = Alkali + Chlorine. The salt may be the chloride of any of the alkali metals. The power for electrolysis (direct current) may be derived from any of the various prime movers driven by steam, coal, gas, oil or water. The alkali produced is usually the hydroxide, but sometimes also the carbonate, of any of the alkali metals.

TABLE 1—DISTRIBUTION OF AMMONIA-SODA PLANTS THROUGHOUT WORLD

World Production 1941: About 7,000,000 Metric Tons of Soda Ash

Country	*No. of Plants*	*Largest Single Plant at*	*Nominal Capacity*
United States	9	Syracuse	2000 Tons/Day
United Kingdom	6	Norwich	1400
Germany	6	Bernburg	1000
France	10	Dombasle	1100
Soviet Union	6	Donetzki (2)	1100
Austria	1	Elbensee	200
Hungary	1	Marosujvar	15
Belgium	1	Couillet	250
Spain	2	Torrelavega	300
Italy	3	Rossignano	700
Canada	1	Amherstburg	200
Czecho-Slovakia	3	Nestomitz	300
Rumania	2	Turda	50
Poland	2	Montwy	150
Yugoslavia	2	Lukavac	100
Switzerland	1	Zurzach	100
Norway	1	Eidanger	75
India	2	Mithapur (Kathiawad)	120
Japan	4	Tokuyama	1000
China	2	Tangku	250
Chile	1	Valparaiso	Less than 1 ton
Venezuela	1	Maiquetia	2
Australia	1	Adelaide	100
Holland	1	Roermond	50

Relative Production of Alkali and Chlorine—With respect to the ammonia soda process there is only one valuable product from the main reaction, since the calcium chloride is in most cases thrown away. Likewise, the amount of soda ash converted to caustic soda is entirely at the option of the alkali manufacturer. On the other hand, with respect to the electrolytic process, caustic soda and chlorine, both valuable products, are produced in the fixed ratio of 40 parts NaOH to 35.46 parts of chlorine and this ratio cannot be varied at the discre-

TABLE 2—DISTRIBUTION OF AMMONIA SODA PLANTS IN THE UNITED STATES AND CANADA

Solvay Process Co., Syracuse, N. Y., Detroit, Mich., and Baton Rouge, La.
Michigan Alkali Co., Wyandotte, Mich.
Columbia Alkali Corp., Barberton, Ohio
Diamond Alkali Co., Painesville, Ohio
Mathieson Alkali Works, Inc., Saltville, Va., and Lake Charles, La.
Southern Alkali Co., Corpus Christi, Texas
Canadian Industries Ltd., Amherstburg, Ont.

TABLE 3—CHLORINE PRODUCING PLANTS IN THE UNITED STATES IN 1941*

1. Brown Company, Berlin, N. H.
2. Mathieson Alkali Works, Niagara Falls, N. Y.
3. S. D. Warren Company, Cumberland, Me.
4. The Dow Chemical Company, Midland, Mich.
** 5. Niagara Alkali Company, Niagara Falls, N. Y.
6. Pennsylvania Salt Mfg. Co., Wyandotte, Mich.
7. The D. M. Bare Paper Company, Roaring Spring, Pa.
8. West Virginia Pulp & Paper Co., Piedmont, W. Va.
** 9. Westvaco Chlorine Products Corp., South Charleston, W. Va.
10. Hooker Electrochemical Company, Niagara Falls, N. Y.
11. West Virginia Pulp & Paper Co., Mechanicsville, N. Y.
12. West Virginia Pulp & Paper Co., Tyrone, Pa.
13. West Virginia Pulp & Paper Co., Covington, Va.
14. Castanea Paper Company, Johnsonburg, Pa.
15. Gulf Oil Corporation, Port Arthur, Texas
** 16. Great Western Division, The Dow Chemical Co., Pittsburg, Calif.
17. Penobscot Chemical Fiber Co., Great Works, Me.
18. Oxford Paper Company, Rumford, Me.
19. Niagara Smelting Corporation, Niagara Falls, N. Y.
** 20. Isco Chemical Company, Niagara Falls, N. Y.
21. E. I. du Pont de Nemours & Co., Deepwater, N. J.
22. Kimberly-Clark Corp., Kimberly, Wisc.
23. Eastern Manufacturing Company, South Brewer, Me.
24. Fields Point Mfg. Corp., Providence, R. I.
25. E. I. du Pont de Nemours & Co. (R. & H.), Niagara Falls, N. Y.
26. Belle Alkali Company, Belle, W. Va.
27. The Champion Paper & Fibre Company, Canton, N. C.
** 28. The Solvay Process Company, Syracuse, N. Y.
29. Monsanto Chemical Company, East St. Louis, Mo.
30. Diamond Alkali Company, Painesville, Ohio
31. Hooker Electrochemical Company, Tacoma, Wash.
32. Pennsylvania Salt Mfg. Company, Tacoma, Wash.
33. Morton Salt Company, Manistee, Mich.
34. Pittsburgh Plate Glass Co. (Columbia Division), Barberton, Ohio
35. The Solvay Process Company, Hopewell, Va.
36. The Solvay Process Company, Baton Rouge, La.
37. Southern Advance Bag and Paper Company, Hodge, La.
38. Southern Alkali Corp., Corpus Christi, Texas
39. The Champion Paper & Fibre Company, Houston, Texas
40. Michigan Alkali Works, Wyandotte, Mich.
41. Hercules Powder Company, Hopewell, Va.
42. Ethyl Gasoline Corporation, Baton Rouge, La.
43. Dow Chemical Company, Freeport, Texas

* Murray, R. L., Trans. Am. Inst. Chem. Eng., *36*, 448 (1940).
** KOH as well as NaOH.

tion of the manufacturer. Thus we come to the important conclusion that the amount of electrolytic alkali produced is controlled by the demand for chlorine. Since the demand for caustic soda is greater than the demand[2] for chlorine (about double in 1939 in the United States) it is seen that the balance of the requirements must be made up from the ammonia soda process. Again, the demand for soda ash (Na_2CO_3) greatly exceeds the demand for ammonia soda

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[2] See Chapter 1.

caustic so that only a small proportion (about 21 per cent in 1939 in the United States) of soda ash is converted to caustic soda.

While most countries have an abundance of raw materials required for the production of alkali there are certain economic factors which govern the successful operation of an alkali plant. With respect to the ammonia soda process, the salt, limestone, and power must be readily available in the immediate vicinity of the alkali plant and these raw materials must be inexpensive and of good quality. To illustrate, some of the most successful operations recently established on the Gulf of Mexico utilize salt from near-by salt domes, lime made from oyster shells dredged from the near-by waters of the Gulf, and natural gas from near-by petroleum producing fields. Adequate transportation facilities are essential and the plant should preferably have good railroad connections and be on deep navigable water. Lastly, the successful alkali plant should be located fairly close to consuming markets. With respect to electrolytic alkali plants the same criteria apply except that lime is not an essential raw material. Cheap electric power is more vital for this process than for the ammonia soda process, consequently many electrolytic plants are found located near a good source of water power or a good source of cheap fuel.

Chlorine without Caustic Soda—In recent years there has been some attempt to produce "chlorine without caustic soda." This is because the demand for chlorine continues to rise at a much greater rate than the demand for caustic soda. Obviously, as long as the demand for chlorine does not exceed that for caustic, the desired shift in production could be made by producing less caustic in connection with the ammonia soda process. But this would have a deleterious effect on the ammonia soda industry which is most essential and by no means obsolete, so there is good economic reason for trying to find means of producing chlorine without having caustic as a by-product.

Fundamentally, however, it is impossible to manufacture chlorine without making an alkali of some kind as a by-product. For example, the electrolysis of fused sodium chloride yields metallic sodium[3] and the electrolysis of fused magnesium chloride yields metallic magnesium; both of these are alkali metals. The nitrosyl chloride process recently introduced in the United States[4] is a method of reacting nitric acid and salt to produce chlorine and sodium nitrate. While sodium nitrate is in itself not an alkali, every ton of sodium nitrate made by the nitrosyl process displaces a ton of sodium nitrate made from soda ash and nitric acid. It is thus seen that this process is not an answer to the problem. Chlorine can be made from hydrochloric acid by electrolysis or by the Deacon process or by oxidation with nitric acid. If the source of the hydrochloric acid is the by-product HCl coming from a chlorine reaction, then this is a step towards a greater utilization of the chlorine originally made along with caustic soda. If the hydrochloric acid derives from salt cake, then this salt cake is really just another source of alkali in so far as the kraft pulp industry is concerned, displacing an equivalent amount of alkali as soda ash. While these so-called "chlorine without caustic" operations may be profitable in some instances for individual companies it cannot be said that anything has been gained for the alkali industry as a whole.

[3] See Chapter 12.

[4] Solvay Process Co., Hopewell, Va.

TABLE 4—PRODUCTION OF SODA ASH IN THE UNITED STATES

From U. S. Census of Manufacture, 1937

Year	*Total Production Short Tons*	*Made and Consumed Same Plant*	*Total Sales Tons*	*Value Dollars Per Ton*	*Ammonia Soda*		*Natural & Electrolytic*	
					Sales Tons	*Number Plants*	*Sales Tons*	*Number Plants*
1921	959,593	183,265	776,328	37.76	746,183	8	30,145	11
1925	1,907,791	539,131	1,368,660	23.56	1,310,882	6	57,778	6
1929	2,682,216	868,360	1,813,856	19.09	1,717,944	6	95,912	8
1933	2,317,011	662,983	1,654,028	14.63	1,585,633	6	68,395	3
1937	3,037,421	713,662	2,323,759	14.52	2,205,006	9	118,753	7
1940 *	3,157,000	785,000	2,372,000	....	2,240,000	.	132,000	.

* Chem. Met. Eng., *48*, 92 (1941).

Production and Distribution of Alkali—In 1939 the consumption of soda ash in the United States was 2,964,000 tons, practically all of which was made by the ammonia soda process. Statistics on the trend of production, the selling price and the number of producing plants is given in Table 4. The distribution of soda ash consumption by industries in the United States is given in Table 5.

TABLE 5—ESTIMATED DISTRIBUTION OF SODA ASH CONSUMED IN THE UNITED STATES *

Consuming Industries	*1940 Short Tons*
Glass	904,000
Soap	182,000
Caustic and bicarbonate	780,000
Other chemicals	710,000
Cleansers and modified sodas	135,000
Pulp and paper	111,000
Water softeners	32,000
Petroleum refining	12,000
Textiles	45,000
Exports	61,000
Miscellaneous	185,000
Total	3,157,000

* Chem. Met. Eng., *48,* 92 (1941).

From this table it is seen that glass is the largest consumer of soda ash, caustic soda second, and other chemicals, chiefly sodium nitrate, third. The production of caustic soda in the United States is given in Table 6. The interesting thing about this table is that it shows the rise of electrolytic caustic soda until in 1939 it equaled the production of lime-soda caustic. The distribution of caustic consumption in the United States is given in Table 7. From this table it is seen that the largest consumer is rayon and cellulose, with chemical use second and soap third.

TABLE 6—PRODUCTION OF CAUSTIC SODA IN THE UNITED STATES *

Year	*Lime-Soda*	*Electrolytic*	*Short Tons Total*
1921	163,044	75,547	238,591
1925	355,783	141,478	497,261
1929	524,985	236,807	761,792
1933	439,363	247,620	686,983
1937 (revised)	488,807	479,919	968,726
1939 (revised)	530,907	494,104	1,025,011
1940 (estimated)	500,000	595,000	1,095,000

* Chem. Met. Eng., *48,* 92 (1941).

USE OF CHLORINE

Because of demand for chlorine, the electrolytic industry has gone forward during the last few years by leaps and bounds. In the ten year period between 1931 and 1940, the output of chlorine was more than doubled and the annual

TABLE 7—ESTIMATED DISTRIBUTION OF CAUSTIC SODA CONSUMED IN THE UNITED STATES *

Consuming Industries	*1940* *Short Tons*
Soap	95,000
Chemicals	220,000
Petroleum refining	88,000
Rayon and cellulose film	230,000
Lye	48,000
Textiles	48,000
Rubber reclaiming	20,000
Vegetable oils	16,000
Pulp and paper	50,000
Exports	105,000
Miscellaneous	175,000
Total	1,095,000

* Chem. Met. Eng., *48,* 92 (1941).

output of electrolytic caustic is now equal to that of lime caustic made from ammonia soda ash. A rough estimate [5] of the uses of chlorine is as follows:

TABLE 8—ESTIMATE OF USES OF CHLORINE

Pulp bleaching	21%
Chlorination products	60%
Disinfectants and sanitation	6%
Textiles	5%
Miscellaneous uses	8%

The percentage consumed in pulp bleaching has decreased from what it was ten years ago. This was because of big increase in the use of chlorine for chlorination and in chemical manufacture, rather than a decrease in its use for pulp bleaching. In 1929 electrolytic caustic output was only a third of the total output of caustic in the United States, but now it is a half. The 1940 total production capacity for chlorine from the electrolytic process in the United States is about 1500 tons of Cl_2 a day; whereas ten years previously it was only 600 tons a day.

THE MANUFACTURE OF SODA

T. P. Hou

The recovery of soda (Na_2CO_3) from natural deposits was discussed in Chapter 9, so the material on soda in this chapter will be confined to the manufacture from sodium chloride.

Historical Survey—The manufacture of anhydrous sodium carbonate, commercially known as soda ash, was formerly exclusively conducted by the LeBlanc process. This process was invented by Nicolas LeBlanc,[6] a Frenchman, who in

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[5] Mantell, C. L., Chem. & Met., *47,* 166, 1940; Chem. & Met., *38,* 88, 1931; and Murray, R. L., Chem. & Met., *47,* 396, 1940.

[6] Lunge, G., "Sulphuric Acid and Alkali," Vol. III, pp. 1–212, D. Van Nostrand Co., New York.

1775, among several others, submitted an outline of a process for making soda ash from common salt, in response to an offer of reward by the French Academy in Paris. LeBlanc's proposal was accepted and found workable on a commercial scale.

The essential reactions in the LeBlanc process are:

$$
\begin{aligned}
NaCl + H_2SO_4 &= NaHSO_4 + HCl\uparrow \\
NaCl + NaHSO_4 &= Na_2SO_4 + HCl\uparrow \\
Na_2SO_4 + 2C &= Na_2S + CO_2\uparrow \\
Na_2S + CaCO_3 &= Na_2CO_3 + CaS
\end{aligned}
$$

Little variation was found necessary, after years of operation, in the proposed proportions of salt, limestone, and coal. Never before was there a process so nearly perfect in the form first outlined by its inventor, subsequent improvements being made only on the mechanical equipment. LeBlanc obtained financial backing and built a plant at St. Denis, near Paris, which was confiscated during the French Revolution.

The development of the LeBlanc soda industry in France was not as rapid as it was in England. James Muspratt was among the English pioneers to introduce LeBlanc's process to England, where the industry was given a great impetus by the removal of the salt tax in 1823, a condition absolutely necessary for the existence of an industry depending on salt for raw material.

LeBlanc's process held its sway for nearly a century, during which large quantities of artificial soda were made by this process. It was, however, gradually superseded by a newer process, and the struggle between the old and the new processes was both instructive and significant. This newer process was in the form of an ammonia soda process.[7]

In England and on the Continent, LeBlanc's process for soda-ash manufacture has now disappeared, while in the United States soda ash has been, from the very beginning, made exclusively by the ammonia process.[8] Nowadays a portion of LeBlanc's process is left in the form of muriatic acid manufacture.[9]

$$
\begin{gathered}
NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \\
NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl
\end{gathered}
$$

and another, without the addition of limestone, in the manufacture of sodium sulfide:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

However, the whole LeBlanc process for the manufacture of soda ash has sunk into oblivion. In the matter of purity, cost of manufacture, labor in handling, and simplicity in the line of products, LeBlanc's process cannot compete with the ammonia process. For the production of caustic soda and bleaching powder, the present electrolytic method possesses all the advantages; nobody today would think of manufacturing bleaching powder from muriatic acid through the intermediate stages represented by the Weldon or the Deacon process.

[7] Hou, T. P., "Manufacture of Soda," A. C. S. Monograph No. 65, Chap. III, Second Edition, Reinhold Publishing Corp., New York (1942).

[8] Trump, E. W., Chem. & Met. Eng., *40*, 126 (1933).

[9] See Chapter 9.

The development which eventually forced the LeBlanc process into discard, came from Belgium. In 1861, Ernest Solvay, the son of a salt manufacturer, observed the reaction of ammonium bicarbonate on brine in his Uncle Semet's gasworks' laboratory, a reaction known for more than twenty-five years before this time. Patents covering this chemical reaction had been taken out before his time, and plants actually built in England and elswhere to work on this principle, though without success. Notwithstanding, Solvay, with confidence in the value of his discovery, built a plant in Couillet, near Charleroi, Belgium, in 1863. Operation began in 1865. For several years, a struggle went on with almost insurmountable difficulties arising from the mechanical working of the process. The plant was constantly in danger of being shut down. Not until 1872 was success assured him, when his works could produce something like ten tons of soda ash a day. Construction of a much larger plant in Dombasle, near Nancy, France, and another one at Norwich, in Cheshire, England, using Solvay's layout and equipment, then followed; and the battle between LeBlanc's process and the ammonia-soda process began, ending in a complete victory for the latter.

OUTLINE OF THE AMMONIA-SODA PROCESS

The ammonia-soda process as developed by Solvay with apparatus of his design is also known as the Solvay process. In employing the same reaction, apparatus has been introduced by Honigmann,[10] Schloesing, Boulouvard, Schreib,[11] and others, but the Solvay type is now almost universally employed. The chemical reactions involved are expressed essentially as follows:

$$NH_4OH + CO_2 \rightarrow NH_4HCO_3 \qquad (1)$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3 \qquad (2)$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \qquad (3)$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O \qquad (4)$$

Chemically, the reactions look very simple. But the control of the process is very difficult, and requires highly scientific training. The practical working is attended with mechanical difficulties arising from the following causes:

1. Ammonia is volatile, and unless the operation is well managed the loss of this expensive reagent is large.

2. The ammonia-CO_2 combination is corrosive at elevated temperatures, especially on steel apparatus, and free ammonia in the liquor excludes the use of copper, brass or bronze in the construction of the apparatus, while the ammonium and sodium chlorides in the liquor are difficult to handle.

3. The working admits of no interruption, so that it is not only a 24-hour-a-day job, but also a 365-days-a-year job; any stoppage throwing off the normal working routine, which cannot be immediately restored.

4. Different divisions of the process are so interlocked that trouble occurring in one division will be reflected in other divisions, and in serious cases may paralyze the whole plant if reserve units are not ready.

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[10] Lunge, G., "Sulphuric Acid and Alkali," Vol. III, pp. 1–212, D. Van Nostrand Co., New York.

[11] Schreib, H., "Die Fabrikation der Soda nach dem Ammoniakverfahren," Julius Springer, Berlin.

Therefore, the industry calls for a group of experienced, intelligent workmen with high skill, quick judgment, and efficient organization.

In what follows, only the Solvay system of operation will be considered.

Preparation of Brine—The process is unique in that salt is introduced in the form of a solution, unlike the LeBlanc process, for which solid salt is required. The source of salt is most commonly rock salt, but to a small extent also sea salt obtained by solar evaporation as in Southern France, China, Japan, and the United States. The supply from the rock-salt mines is either in the form of natural or artificial brine. Natural brine is formed by underground water flowing through a bed of the rock-salt deposits. It may be called an artesian brine. Good natural brine contains salt almost up to theoretical saturation. Such brine occurs notably in the Cheshire district, England. Artificial brine results from a method of mining salt with water, and, fortunately, is exactly in the form required by the ammonia soda works. The methods used in obtaining brine are described in Chapter 9.

Sea brine contains many impurities, but fortunately the crystallization process eliminates some of them, especially calcium and magnesium salts, so that sea-salt crystals are better adapted to ammonia-soda manufacture than saturated brine direct from sea water. Natural brine or artificial brine from rock-salt deposits, contains as its principal impurity calcium sulfate (gypsum), while sea brine contains, in addition to calcium, considerable amounts of magnesium. Table 9 shows the compositions of rock salt and of sea-salt crystals, which contain less magnesium salts than the original sea brine.

TABLE 9—COMPARISON OF ROCK SALT AND SEA SALT

Rock Salt	*Per Cent of Solids*	*Sea Salt Crystals*	*Per Cent of Solids*
Moisture	0.34	Moisture	7.66
Insoluble matter	0.01	Insoluble matter	0.50
$CaSO_4$	1.69	$CaSO_4$	1.33
$MgCl_2$	0.16	$MgCl_2$	0.78
$CaCl_2$	0.18	$MgSO_4$	0.06
NaCl	97.62	NaCl	89.67

From the above, it can be seen that rock salt as the raw material for ammonia-soda manufacture is superior to sea salt. This will be better appreciated when it is remembered that magnesium precipitates are as a rule more difficult to settle out in the process of ammoniation. (See below.)

Solution of Ammonia in Saturated Brine or "Ammoniation of Saturated Brine"—Instead of introducing ammonium bicarbonate to the brine, as would appear from the above chemical equations, in actual practice advantage is taken of the solubility of ammonia gas in water and therefore in brine, and so ammonia gas is first introduced into the brine. Then, and only then is CO_2 gas passed in to make ammonium bicarbonate in solution. A little thought will show that it would be impossible to introduce CO_2 into the brine first, and then ammonia; for in the absence of OH ions, i.e., alkalinity, little CO_2 gas can be dissolved in the brine except at extremely high pressures. Furthermore, the introduction of ammonia gas into brine serves to impart not only the necessary concentration of ammonia but also to purify the brine, a step very essential to the extreme degree of purity so highly valued in ammonia-soda ash.

This step is carried out in an ammonia absorbing apparatus or "absorber" (Figure 1), where saturated brine coming from different ammonia washers (scrubbers) flows down from the top over a number of distribution plates consisting of "mushrooms" and division plates; while ammonia gases enter at the bottom and bubble up through the downcoming brine, with vacuum pulling the gases through. These ammonia gases come from the ammonia still or "distiller" (Figure 2) and pass through heat exchangers or coolers in which feed liquor is preheated, and then through partial condensers in which water is used as the cooling medium, the purpose being to condense out steam from ammonia gases by partial condensation (Figure 3).

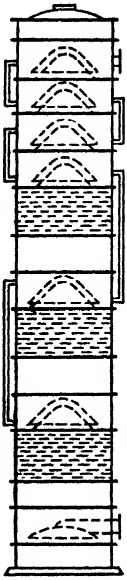
FIG. 1. Ammonia Absorption Apparatus.

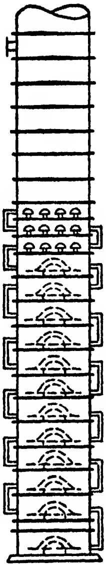
FIG. 2. Ammonia Still.

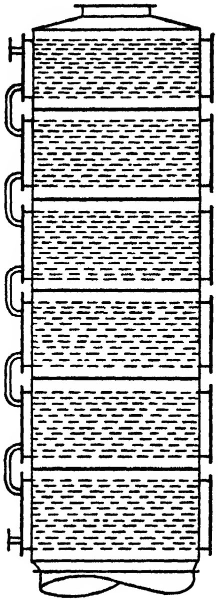
FIG. 3. Partial Condenser.

This "distillation" operation is essentially the carrying out of reaction (4) above. It is the same operation that is used for the total recovery of ammonia in by-product coke plants.[11a] These ammonia gases contain, besides ammonia and steam, considerable CO_2 and some H_2S, which, in combination with ammonia, form $(NH_4)_2CO_3$, NH_2COONH_4, NH_4HCO_3 and NH_4HS. The introduction of this $(NH_4)_2CO_3$ and excess of NH_3 gas to the brine has exactly the same effect on the brine as the soda-lime treatment. As a consequence, calcium is thrown down as $CaCO_3$ and magnesium as $MgCO_3$ or basic magnesium car-

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[11a] See Chapter 15. The equipment used in the ammonia-soda process is described on p. 417.

bonate, and a triple salt, $MgCO_3 \cdot NaCl \cdot Na_2CO_3$.[12] Further, the heat of solution of ammonia gas in the brine, coupled with heat from the condensation of steam, brings the resultant brine temperature to around 70° C. and creates a very favorable condition for treating the brine in the hot solution.

The brine that has taken up the necessary amount of ammonia is allowed to settle in large vats consisting of three units or more per series, and the clear liquor from the final overflow, after passing through the final coolers (called vat coolers), is pumped to the tower house for making sodium bicarbonate. It is truly said that good soda ash is made in the absorber and vat system; for any impurities left in the ammoniated brine, i.e., any calcium and magnesium salts or any unsettled-out solids in the brine, will surely find their way to the final product as insoluble matter in the soda ash. Experience shows that anything less than 0.10 g. total insoluble matter per liter in the ammoniated brine will make good soda ash.

Chemically, the ammoniation of brine is very simple; mechanically, it is attended with many difficulties. The system must be tight and under vacuum. The gravity flow of brine must not be interfered with by the vacuum, or suspension of brine flow would result. Separation of solids or "mud" in the apparatus and around the overflow pipes tends to plug the brine passage. The mud, especially that from the magnesium compounds from the sea brine, adheres to the surface and gradually forms an incrustation constricting the brine passage. To avoid interruption of operation, a duplicate set of units and piping system must be provided for changing-over and cleaning after a certain interval. This cleaning schedule is peculiar to each individual plant.

Ammonia absorption[13] is a function of temperature. Unfortunately, considerable heat is developed during ammonia absorption and from condensation of steam. If the temperature is allowed to rise excessively, the vapor tension of ammonia is increased, and much ammonia gas will be driven out and passed on to the top or even out of the system, creating a condition of "hot-top" in the absorber system. It is found that the temperature of the exit gas from the absorber top, entering the washer, should not be permitted to rise much above 35° C. Hence cooling is very essential in ammonia absorption. In practice, methods for cooling both the liquor and the gas are employed at points most suitable. Unfortunately, neither of these methods of cooling is very satisfactory. Gas cooling is not efficient, especially as crystals of ammonium salts are likely to adhere to the cooling tubes, and sulfide scale is formed on the metal surface in contact with the gas. If proper attention is not given and the temperature gets too low, blocking up of the whole cooling section may occur from formation of ammonium carbamate, ammonium carbonate, and ammonium bicarbonate crystals. These salts all arise from the presence of CO_2 in the system, even though equation 4 (above) does not indicate its presence. It will be observed, however, that this NH_4Cl solution which is being decomposed, results

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[12] Hou, T. P., "Manufacture of Soda," A. C. S. Monograph No. 65, Chap. VII, "Ammoniation of Saturated Brine," second edition, Reinhold Publishing Corp., New York (1942).
Also Wilson, E. O., and Chiu, Y. C., Ind. Eng. Chem., *26*, 1099 (1934).
See also Chapter 6.

[13] For a discussion of the principles of gas absorption see Chapter 2, p. 65, also Sherwood, T. K., "Absorption and Extraction," McGraw-Hill Book Co. (1937).

from reaction 2, wherein $NaHCO_3$ is also formed. At least some $NaHCO_3$ and the excess of NH_4HCO_3 dissolved will remain in the liquid when it is recirculated for the release of NH_3 and will be partially decomposed in the distilling tower, with the release of CO_2.

The analysis of a typical sample of the crystals deposited from the ammonia gases in the cooling system is given in Table 10.

TABLE 10—COMPOSITION OF AMMONIUM CARBONATE CRYSTALS

	Per Cent
Ammonium carbonate, $(NH_4)_2CO_3$	47.61
Ammonium carbamate, $NH_4NH_2CO_2$	42.23
Ammonium bicarbonate NH_4HCO_3	8.80
Ammonium chloride, NH_4Cl	1.04

In cooling the liquor, scale formation in the cooling tubes due to mud deposit gradually insulates the metal surface against heat transfer, putting the coolers out of commission. This then necessitates opening up the cooler for cleaning, for which purpose boiling out with steam is the most effective treatment. The composition of a typical sample of the mud from sea salt is given in Table 11.

TABLE 11—COMPOSITION OF MUD

	Per Cent
$MgCO_3$	20.27
$NaCl$	19.75
$NaHCO_3$	17.89
$CaCO_3$	11.50
NH_4HCO_3	10.23
$(NH_4)_2CO_3$	4.58
$(NH_4)_2SO_4$	2.53
Fe_2O_3	0.43
FeS	0.25
Al_2O_3	0.25
SiO_2	0.07
Free NH_3	0.06
K_2CO_3	0.23
Water (by diff.)	11.96

It is interesting to note that NaCl precipitates with $MgCO_3$ in the mud in the form of a double salt, or as a triple salt $NaCl \cdot MgCO_3 \cdot Na_2CO_3$.

In plant parlance, the concentration of ammonia or chlorine is expressed in "titres," a titre being 1 c.c. of a normal solution taken by a 20-c.c. sample for titration. Ammoniation of brine stops when the ammonia titre shows 98-99 in the resulting ammoniated brine, which should then possess a concentration of NaCl titre of about 90 (in terms of chlorine titre).

To avoid troublesome mud formation in the absorber, vats and cooler system, it has become a practice in certain ammonia-soda plants to pretreat the brine before it is sent to the system. This is done by the use of the reagents, soda ash and lime, in the cold, or by a pretreatment with ammonia to remove calcium and magnesium. This treatment for the purification of brine was given in detail in a previous chapter.[14]

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[14] Chapter 9.

This treatment of the brine renders the operation of the absorber system very efficient and smooth, and greatly minimizes the cleaning operation in the absorber, vats or coolers, thereby saving considerable labor in the removal of the scale and preventing frequent interruption of operation due to the necessity of changing over to the stand-by units. A great saving in salt is also effected by not having to pump such a large volume of mud to the distiller from the settling vats. Such pretreatment of the brine has practically done away with the cleaning schedule necessary for the absorber and vat system and has so greatly increased the working capacity that the practice is being more and more generally adopted in all the ammonia-soda plants.

Carbonation of Ammoniated Brine—After the brine is saturated with ammonia, it is necessary to saturate it with CO_2 to promote reactions (1) and (2) (p. 410). This absorption is carried out in a column, which will be described later. The following reactions occur in the column:

$$NH_4OH + CO_2 \rightarrow NH_4HCO_3 \text{ (with excess of } CO_2\text{)}$$
$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

This is a case of gas absorption followed by a chemical reaction in solution.[18] As is usually the case in such systems, the gas absorption is relatively slow and the second, ionic reaction is relatively rapid. Hence, the rate of CO_2 absorption controls the rate of the combined overall reversible reaction:

$$NH_4OH + CO_2 + NaCl \rightleftarrows NaHCO_3 + NH_4Cl \qquad (5)$$

Source of CO_2. There are two sources of the CO_2 which is used in the ammonia-soda process: (1) The decomposition of $NaHCO_3$ to produce Na_2CO_3 according to reaction (3) above. This is carried out in the apparatus called the "dryer," in the parlance of the industry. This dryer gas will contain 90 to 95 per cent CO_2. (2) By the decomposition limestone according to the reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

The kilns used in the process are built and operated with special precautions to produce as high a concentration of CO_2 as possible. In practice, 41 to 43 per cent of CO_2 is obtained in the kiln gases, with very little CO or O_2, the rest of the gas being N_2.[15]

The Absorption Tower. After settling and cooling, the ammoniated brine, which is now of yellowish green color and free of dark residue, is sent to the carbonating towers by means of centrifugal pumps. The tower (Figure 4) is essentially a tall cast-iron cylinder, 6 ft. inside diameter (sometimes 7′-6″ dia.) and about 75 ft. from the base to the top of the cover, divided into a number (as many as 36) of sections, with a gas distribution passette between each ring. The lower rings have cooling boxes with horizontal, multiple-pass cast iron cooling tubes.

The ammoniated brine or "green liquor" enters near the top (3-4 rings from

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[15] For a description of the type and operation of the continuous shaft kilns used in lime burning, see Chapter 22.

For the complete description of the special features of lime kilns used for the ammonia-soda process, see Hou, T. P., "Manufacture of Soda," A. C. S. Monograph 65, Chapter VI, Reinhold Publishing Corp., New York (1942).

the cover) and the CO_2 gases at the bottom, countercurrently. The bicarbonate suspension or "draw-liquor" is tapped from the bottom, but is piped up to about 40 feet from the base, where filters are located, and the suspension is filtered.

The gas representing, in the ordinary arrangement, a mixture of the "rich" CO_2 (or dryer gas) and a comparatively dilute CO_2 (or "lean" gas) from lime kilns, is pumped into the columns by CO_2 compressors at a pressure of 34-36 lbs. per sq. in. The waste gas from the top of the columns, containing 2-4 per cent CO_2 by volume, is scrubbed free of ammonia in the so-called "tower washer," a scrubber, using fresh brine, and then exhausted to the air. This mixed gas going to the columns contains from 53 to 65 per cent CO_2, depending upon the rate of dryer operation with respect to column operation, and the richness of the dryer gas and of the lime kiln gas.[16] The exhaust gas from the vacuum pump or "exhauster" from the absorber system (mentioned above) should contain rich CO_2 gas, if the system is kept air-tight, and is best returned to the columns here through the compressor intake. According to the strict countercurrent principle, the very rich "dryer" gas containing 90-95 per cent CO_2 should enter as such into the very bottom of the columns where sodium bicarbonate slurry is to be drawn out, while the "lean" gas containing 41-43 per cent CO_2 should enter at four or five rings up, where the partial pressure of CO_2 in the gas phase corresponds to this lean gas. This double entry of CO_2 gases is sometimes provided.

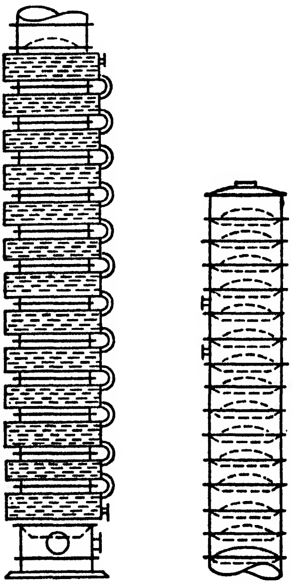

FIG. 4. Absorption Tower.

Concentration of Reactants in Tower. The reaction taking place in the tower (equation 5) is reversible. The yield of $NaHCO_3$ and NH_4Cl is obviously dependent on the mass action effect, so it is important to keep the concentration of the reactants as high as possible. Unfortunately, in the process of ammoniation, increase in volume of brine, due to ammonia absorption and to admixture of steam condensate, lowers the sodium chloride concentration in the resulting ammoniated brine so that it is less than 94 per cent of the theoretical saturation, even taking into account the decrease in solubility of NaCl in the presence of ammonia at the concentration employed. The addition of solid salt after ammoniation, to bring the resulting ammoniated brine to full saturation with respect to NaCl, is not practiced because of mechanical difficulties.

The next factor is the concentration of CO_2 in the gas. Efforts are made in ammonia-soda plants to maintain the richness of both the dryer and kiln gases. When the dryer gas is mixed with the kiln gas in the compressor intake, the resulting mixture under best conditions cannot average more than 65 per cent

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[16] Hou, T. P., "Manufacture of Soda," A. C. S. Monograph No. 65, Chapters VIII and IX, second edition, Reinhold Publishing Corp., New York (1942).

Ibid., Chapter XXVI, "Losses and Consumption of Raw Materials in Ammonia-Soda Process," see calculations for mixed CO_2 gases.

CO_2. If the dryer gas is separately introduced, its original 90 per cent CO_2, or more, is preserved. The countercurrent principle demands this separate entry, which gives good results, although the arrangement is somewhat more complicated.

The third factor is the concentration of ammonia. It is comparatively easy to increase the concentration of ammonia, as the resulting ammoniated brine contains only 8 per cent NH_3 by weight. But unless ample cooling area is provided in the absorber, any attempt to increase ammonia titre entails corresponding decrease in the chlorine titre in the resulting ammoniated brine.

In practice, because of the difficulties due to scale formation, etc., in the ammoniation of saturated brine, an efficient cooling is not easily arranged. Further, a large excess of NH_3 in the ammoniated brine may cause excessive NH_4HCO_3 crystals to separate with $NaHCO_3$ in the columns. A slight excess of NH_3 is, however, desirable, as a certain amount is always blown to the tower washer with the exit waste gases by the gas-distillation effect and becomes unavailable for reaction in the columns. In terms of the number of equivalents per liter, ammonia excess is about 8-10 per cent over chlorine, chlorine titre being taken to represent sodium, simply because Cl^- is more readily determined than Na^+. For instance, with a Cl^- titre of 89-90, the free ammonia titre in the ammoniated brine should be 98-99.

Effect of Temperature on the Reaction. The fourth factor which is even more far-reaching in its effect is the temperature gradient in the column. This has a direct bearing on the cooling capacity of the column, on the distribution of cooling surface in the column, on the temperature of green liquor in the feed, and on the temperature of CO_2 gases from the compressor. In the reversible reaction of equation (5) equilibrium is rapidly shifted to the left by a rise of temperature. Low initial temperatures in the reacting components (the ammoniated brine and CO_2 gases) and a thorough but gradual cooling in the column as the liquor descends, are very essential to column operation. The supposition that cooling to too low a temperature would cause poor crystal formation in the bicarbonate obtained, is erroneous.

With a gradual cooling, from a high reaction temperature (55°-60° C.) in the upper part of the column roughly at about two-thirds of the height, and with proper concentrations of ammonia and NaCl in the ammoniated brine, and of CO_2 in the gases entering the column, both at 30°-35° C., there is no theoretical low limit for the temperature of the draw liquor, the practical limit being the ability to cool with the amount of cooling surface provided, the condition of these cooling tubes, and the temperature of the cooling water available. Under such conditions, the lower the draw temperature, the better the "decomposition," and the smaller the loss of ammonia from exposure of draw liquor to the air.

In the original Solvay design, outside cooling of the carbonating tower by sprinkling water around the sides from the top down was employed. William B. Cogswell in 1887 introduced a system of internal cooling with horizontal tubes inserted in each section. A later development employs a very large number of 2-in. cast iron tubes with multiple passes for cooling water in each individual section, giving a longer course for water travel and a longer time of contact with the liquor. This results in a more gradual cooling, better economy in the use of cooling water, and lower draw temperature. In this way, a draw temperature of 21°-22° C. can be maintained with free ammonia at or below 20 titre, giving excellent settling test for the bicarbonate crystals. Poor crystals are obtained when starting a cold column, i.e., a column just changed from cleaning to making, or when normal column operation is interrupted, e.g., when gas to the columns for some reason becomes low in CO_2.

Cleaning the Columns. After working for a period of about 4 days, these columns become dirty, the cooling tubes being coated with so much bicarbonate that efficient cooling cannot be obtained and the low draw temperature cannot be maintained. Cleaning is then necessary. Previously, cleaning was done by shutting down the column and boiling out with steam. This threw off the normal working conditions and seriously interfered with the operation. Fortunately, this drastic treatment is no longer necessary. At present it is found sufficient to run the ammoniated brine, or green liquor, through the dirty column, taking a limited amount of CO_2, usually in the form of "lean" gas, with cooling water cut out. The liquor in this column is carbonated up to, but below, the precipitation point of sodium bicarbonate and the temperature in the column is maintained at 38°-40° C. The CO_2 gas in this precarbonated liquor is maintained at or below 65 c.c. per 2 c.c. sample of the liquor (reduced to atmospheric presssure and room temperature). This stage of carbonation roughly corresponds to the following reaction:

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

From the cleaning column the precarbonated liquor is sent to the other (making) columns by a CO_2 lift. Usually four such making columns take their feed from one cleaning column, so that out of five columns in a group there is one cleaning every day. The period of cleaning varies from 18 to 24 hours. This limited carbonation serves to warm up the liquor by the heat of reaction, to agitate the liquor in the column and thus aid solution of $NaHCO_3$ by the ammoniated brine, and incidentally to precarbonate the liquor for the final carbonation in the other four making columns. In practice, it is found that cleaning is more effective when one cleaning column serves some four making columns, i.e., to run the volume of ammoniated brine taken by four working columns through one cleaning column. The minimum desirable should be three making columns to one cleaning. This sets the modern unit or "element" for an ammonia soda plant at a minimum capacity for economic operation of 150-200 tons per 24 hours.

Filtration of Sodium Bicarbonate—The draw liquor from the columns, containing precipitated sodium bicarbonate in suspension, is next filtered. The bicarbonate crystals belong to the monoclinic system, but the crystals are so fine that, at 800 times magnification under a microscope, they are seen only as rodlike irregular particles. From the manner of formation, these crystals must necessarily be small because of the violent agitation in the column.

The old-style filter consisted of a box with a false bottom over which a layer of felt was placed as the filtering medium. Suction was applied to the closed compartment under the false bottom. The next development was the use of a rotary drum filter. The drum was partially submerged in a basin containing the bicarbonate suspension. Vacuum was maintained inside the drum, and the whole cage outside was covered with a woolen blanket as the filtering medium.

A scraper knife was provided at the edge of the basin to scrape off the thin layer of bicarbonate from the periphery. This method is continuous as long as the pores in the blanket are not clogged, but in an interval of about 15 minutes vacuum had to be cut off and compressed air applied to blow back the blanket from the inside. This semi-continuous drum filter, while representing a great improvement over the old open-tank filter, left much to be desired. Later development in this type of filter is a self-blowing, continuous drum filter.[16a]

As the crystals are formed in the brine, some salt (NaCl) will always be included. To wash out this salt and keep it to a minimum, good soft water is applied in thin films to the bicarbonate layer on the face of the drum. Any NaCl as such, or NH_4Cl left in the bicarbonate, will give rise to NaCl in soda ash; for in the dryer the NH_4Cl will produce NaCl by the reverse reaction:

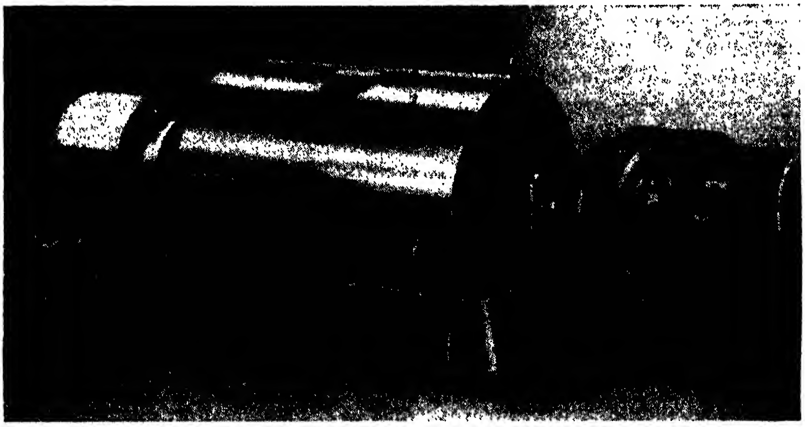

FIG. 5. Continuous Centrifuge. (Courtesy Bird Machine Co.)

$$NH_4Cl + NaHCO_3 \rightarrow NaCl + NH_3 + CO_2 + H_2O$$

Ammonium salts, such as NH_4HCO_3, etc., occluded by the crystals from the mother liquor, are not so objectionable, as they are decomposed and driven out with CO_2 gas in the dryers. Any unprecipitated or unsettled magnesium or calcium compounds in the ammoniated brine will show up in the bicarbonate, and consequently in soda ash. The crystals show a slight bluish cast on account of the presence of traces of the sulfide.

Centrifuges are also used to a certain extent for separating the crystals from the solution. The ordinary basket centrifuge calls for intermittent operation and hence has small capacity. A satisfactory continuous type, self-discharging centrifuge is shown in Figure 5.

There are two types of continuous centrifuges: one is a strictly continuous machine taking the slurry continuously and discharging the bicarbonate continuously, and the other is the automatic intermittent machine charging and discharging intermittently but the cycle is automatically controlled electrically, and the unloading operation done without reducing the speed. Such machines, espe-

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[16a] For a description of the operation of this type of filter, see Chapter 2.

cially the latter (automatic type), are being increasingly introduced into the soda industry. Centrifugal machines can give dryness of the sodium bicarbonate of 8 per cent or less, while well-designed rotary vacuum filters, working on good coarse crystals of sodium bicarbonate, generally give no better than 12 per cent free moisture, though the output per unit is much larger. The high degree of dryness in the bicarbonate obtained from the continuous centrifuge would make this type very desirable to the ammonia-soda manufacturers, who spare no effort to reduce the moisture content in the bicarbonate; because a difference of a few per cent moisture makes a great deal of difference in the drying quality of the bicarbonate and consequently in the operation of the dryers. But compared to the high-yield filters today which have a capacity per unit anywhere from 200 to 500 tons of soda ash per day, these automatic centrifuges have very small capacities and require a much larger capital investment for the same amount of work required. Whether the saving from the greater dryness warrants this, is a matter for the consideration of the individual ammonia soda plants.

The "dryness" of the crude bicarbonate is not directly measured by its moisture content, but indirectly by the amount of soda ash it will yield. This per cent of soda ash is called the "yield" of the bicarbonate in plant parlance. Pure, dry sodium bicarbonate would have a yield of 63 per cent. Ordinary bicarbonate from self-blowing high-yield continuous rotary drum filters has a yield of 54-56 per cent, representing a moisture content of 12-13 per cent. With centrifuges it is possible to get as much as 58 per cent yield, representing only 8 per cent moisture, so that these centrifugal machines, when properly adapted to the ammonia-soda industry, may revolutionize the drying operation in soda ash manufacture.

A complete chemical analysis on a typical sample of the sodium bicarbonate from continuous rotary drum filters is shown in Table 12:

TABLE 12—COMPOSITION OF FILTER BICARBONATE

	Per Cent
$NaHCO_3$	75.60
Na_2CO_3	6.94
NH_4HCO_3	3.42
NaCl	0.39
$MgCO_3$	Trace
Na_2SO_4	0.10
$CaCO_3$	Nil
Water (by diff.)	13.55
Yield	54.64

Decomposition of Sodium Bicarbonate into Soda Ash or "Drying"—The bicarbonate from the filters is next calcined to soda ash. This calcining operation is attended with many mechanical difficulties. The mechanical difficulty would not be so great, were it not for the recovery of CO_2 gas, which requires a closed system.

In decomposing sodium bicarbonate, ammonia, either as such or in the form of NH_4HCO_3, $(NH_4)_2CO_3$, NH_4Cl, is driven out along with the moisture. Then come CO_2 and water from the decomposition of sodium bicarbonate into normal carbonate. It is easy to drive out moisture and ammonia, but the last trace of

CO_2 is driven out with some difficulty. Hence it is necessary to control the temperature of the outgoing soda ash at the discharge or "extract" end of the dryer. It is found that at above 160° C. the ash might be free of bicarbonate, but 180° C. is a more conservative figure to insure complete decomposition of bicarbonate in the ash. In neither the rotary dryers nor Thelen pans is countercurrent heating employed, but in each case bicarbonate is fed at the furnace end and leaves at the end most remote from the fire. There are various reasons for this arrangement; first, it is desired to apply heat at the place where most decomposition is done; second, the intense heat would cause fusion of soda ash if the fire were located at the "extract" end; and third, too much heat would be left in the ash, causing loss of heat and difficulty in cooling, unless an elaborate ash cooler were used.

Mechanically, the procedure in the dryer room is as follows: The bicarbonate from the filters drops onto a belt conveyor system, is fed to each dryer through a feed table (a machine regulating a uniform feed of bicarbonate under a closed system), and, after calcining, comes out as soda ash at the extract end. A portion of soda ash is diverted to the feed end for returned ash and the rest conveyed to the packing bin through a cooler or conveyor (see below), bringing the ash to below 90° C., to be directly packed into gunny sacks or wooden barrels, or else stored in a concrete silo.

Conveying of soda ash is done in a system of closed screw conveyors and enclosed continuous-type bucket elevators. Cooling of the hot ash is generally done in a system of air-cooled screw conveyors or in a water-cooled rotary cooler.

Normal soda ash made by the ammonia process has the composition shown in Table 13.

TABLE 13—COMPOSITION OF LIGHT ASH

	Per Cent
Moisture	Nil
Na_2CO_3	99.2
$NaHCO_3$	Nil
NaCl	0.4 -0.6
Insoluble matter	0.02 -0.04
Fe_2O_3	0.001-0.002

This is known as 58 per cent ash containing about 58 per cent Na_2O. Excess of insoluble matter will cause cloudiness in soda solution. Excessive iron content will discolor the ash rendering it reddish. When the ash has been stored for some time, both moisture and $NaHCO_3$ may be present to a small extent and the ash becomes lumpy. This is due to the formation of the monohydrate and sesquicarbonate in contact with the atmosphere.

The gas from the dryer comes out through an uptake located at the feed end of the dryer, passes through a separator and a gas scrubber where the entrained soda dust is washed out by a down-stream of filter liquor, and is finally cooled in a condenser provided with cooling tubes, and further in a scrubbing tower in direct contact with sprays of cold soft water which scrubs out ammonia from the gas and cools it further to about 30° C. on its way to the CO_2 compressor intake.

The ash thus made is the light ash and has a bulk density of a little more than 0.5, i.e., 32-35 lb. per cu. ft. when loosely filled. With such a light ash, packing cost would run high, and for certain industries, such as the glass industry, etc., light ash is not desirable. The glass industry particularly requires a coarser and denser ash because light ash would reduce the holding capacity of the melting pots and also cause dust losses. For export, freight on the light ash would amount to a big item, so dense ash is also preferred in the export trade.

Soda dust such as collects in the cyclone separators installed in the gas up-take from the dryers, or such other places, is even lighter and is sold as extra light ash, such as the "Fluf" among Solvay products, which is favored by certain buyers who want large bulk in their packing.

For reasons given above, it is necessary to work the ash over again for a denser product. In earlier days, this was done by bringing the ash to an incipient fusion in a reverberatory furnace using gas firing. The present-day practice is to wet the ash with water and dry it again in a rotary. This furnace is exactly the same as the rotary dryer for light ash, except for the feeding end and the gas (steam vapor) handling arrangement. The light ash is wetted with about 16 per cent water by weight and is mixed thoroughly in a screw mixer and fed with a stream of returned dense ash at the intake to the dense ash dryer. The principle of wetting the light ash and drying it again is to bring about physical conglomeration through the formation of $Na_2CO_3 \cdot H_2O$ by the absorption of water, in which form it leaves after re-drying, and the product thus becomes more dense. Ordinary dense ash has about twice the density of the light ash, its density, when determined by loose filling, being 64-67 lb. per cu. ft. Dense ash carries a little higher content of iron, having 0.003-0.005 per cent Fe_2O_3, from re-furnacing. It is packed in bags or barrels containing 500 lbs., while light ash is packed in 200-lb. bags or 300-lb. barrels.

Recovery of Ammonia—Ammonia is a comparatively expensive material, its price as ammonium sulfate carrying 25 per cent NH_3, being about twice that of soda ash, although it is generally supplied to ammonia soda works in the form of crude ammonia liquor containing about 18 per cent total NH_3, including 15 per cent $(NH_4)_2S$. Unfortunately, this reagent is volatile, so that unless the plant is properly equipped and well managed its loss would be serious. One of the main reasons for the failure of the early pioneers in working out the ammonia process was this excessive loss of ammonia. It is very essential to cut down the loss to a minimum. In large plants, the loss nowadays is less than 2-4 kg. (as $(NH_4)_2SO_4$) per ton of soda ash made.

The ammonia which is in the solution from which $NaHCO_3$ has crystallized must be released as a gas, so it can be used to ammoniate more brine. In addition, the ammonia must be removed from the crude liquor which is used to make up the losses from the system. The NH_3 in these solutions may be either "free" or "fixed." Free ammonia is that which is in the form of easily decomposed compounds such as NH_4OH or NH_4HCO_3 and can be released from solution by boiling. Fixed ammonia is that which is in the form of the more stable compounds such as NH_4Cl. It is released from solution by boiling in the presence of a stronger base. The ammonia still makes provision for the recovery of both free and fixed ammonia. While this operation is nearly always termed "ammonia distillation" it is really a desorption or stripping operation. The carrier gas is exhaust steam which is fed into the column.

The mother liquor returning as filtrate after the $NaHCO_3$ crystals have been separated has the approximate composition shown in Table 14.

TABLE 14—COMPOSITION OF MOTHER LIQUOR

Sp. gr. at 15° C.	1.137
NH_4Cl	190 g/l
Free NH_3 (calc. as NH_4HCO_3)	80 g/l
NaCl (unconverted)	75 g/l
$NaHCO_3$ in solution (cir.)	10 g/l
Total CO_2	40 g/l

The mother liquor from the filters diluted with about 6-10 per cent wash water is known as "filter liquor." The wash water dissolves some bicarbonate from the filters. The dilution of mother liquor by wash water is dependent upon the relative amount of water used in washing, which in turn is dependent upon the crystalline character of the bicarbonate from the columns and the rate of filter operation.

The filter liquor is piped to the distiller house, receiving various ammonia condensates and ammonia-bearing liquors on its way. Mixed with streams of sodium sulfide solution and ammonium sulfate solution or crude ammonia liquor from gas works, as the case may be, it is fed to the distiller through centrifugal pumps.

Construction of the Distiller. The ammonia still or "distiller" (Figure 2) is a tall affair consisting of cast-iron sections, 8 ft. inside diameter. The whole distiller is made up of three main divisions, the condenser and the cooler (or liquor preheater), the heater, and the lime still, one on top of the other, so that the overall height is frequently more than a hundred feet. The function of each of the three main divisions (condenser, heater and lime still) is one of dephlegmation by partial condensation to obtain drier ammonia gas; of decomposition of "free ammonia" compounds by heat and distillation of NH_3 by steam; and of converting fixed ammonia by lime and distilling off NH_3, respectively.

The gas from the lime still passes directly through the heater and then through the partial condenser and cooler. This arrangement is economical in floor space but the principle is not sound. The rich ammonia gas from the lime still is never in equilibrium with the liquor in the heater, with the result that some of the ammonia liberated in the lime still may be redissolved in the heater liquor, and the liquor leaving the bottom of the heater contains a considerable amount of free ammonia at the inlet to the prelimer (see below), carrying with it much CO_2 which is liberated with difficulty in the presence of strong ammonia.

The condenser and the cooler (or liquor preheater) consist of a large number of 2-in. cast iron tubes using water and feed liquor as the cooling media, respectively, with outgoing ammonia gases and condensing steam outside, and liquor inside the tubes. The heater is packed with tiles or coke about 6-in. size for a height of 25-30 ft., provided with three passettes below, through which liquor runs down in intimate contact with the upward flowing steam. The lime still consists of a number of steam distributing division plates and "mushrooms," subdividing steam bubbles through shallow depths of a mixture of heater liquor and milk of lime. The number of passettes or plates provided in the lime still determines the concentration of ammonia remaining in the liquid leaving the column.

Obviously, for economy of operation, this must be kept as low as possible, so an ample number of plates must be provided.

Between the heater and the lime still there is generally a lime-mixing tank or "preliming tank" provided with a stirrer which thoroughly mixes the lime with the liquor. At the conical bottom of the preliming tank there is a centrifugal pump sending the "sand" from the bottom of the tank to the distiller. The preliming tank is of such capacity as to allow considerable time for the lime to react before the mixture overflows from the top to the lime still.

The outgoing ammonia gas is cooled and condensed to eliminate as much steam as possible by partial condensation, in order to avoid excessive dilution of brine in the absorber. The condensate, since it contains considerable ammonia, is returned to the distiller.

Reactions in the Distiller. In the heater, "free ammonia" is driven out by the heat of the steam. The term "free ammonia" includes not only NH_3 or NH_4OH, but also NH_4HCO_3, $(NH_4)_2CO_3$, $(NH_4)HS$, etc., so that the reactions taking place in the heater are:

$$NH_4OH \rightarrow NH_3\text{ (gas)} + H_2O \tag{6}$$

$$NH_4HCO_3 \rightarrow NH_3\text{ (gas)} + H_2O + CO_2\text{ (gas)} \tag{7}$$

$$(NH_4)_2CO_3 \rightarrow 2NH_3\text{ (gas)} + H_2O + CO_2\text{ (gas)} \tag{8}$$

$$NH_4HS \rightarrow NH_3\text{ gas} + H_2S\text{ (gas)} \tag{9}$$

The sodium bicarbonate dissolved in the mother liquor or by wash water gives:

$$NaHCO_3 + NH_4Cl \rightarrow NaCl + NH_3\text{ (gas)} + H_2O + CO_2\text{ (gas)} \tag{10}$$

Soda dust dissolved by the filter liquor in the furnace-gas scrubber gives the reaction:

$$Na_2CO_3 + 2NH_4Cl \rightarrow 2NaCl + 2NH_3\text{ (gas)} + H_2O + CO_2\text{ (gas)} \tag{11}$$

If sodium sulfide solution has been added to the filter liquor, the following reaction takes place:

$$Na_2S + 2NH_4Cl \rightarrow 2NaCl + 2NH_3\text{ (gas)} + H_2S\text{ (gas)} \tag{12}$$

The liquor from the bottom of the heater should contain very little or no CO_2 in solution, but considerable free NH_3, for reasons stated above.

In the preliming tank, milk of lime reacts with fixed ammonia:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3\text{ (gas)} + 2H_2O \tag{13}$$

If ammonium sulfate solution is employed instead of crude liquor to replenish the loss of ammonia in the cycle, calcium sulfate is formed in place of soluble calcium chloride:

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_3\text{ (gas)} + 2H_2O \tag{14}$$

The distiller liquor must be maintained at above 90° C.; otherwise troublesome calcium sulfate scale may be formed in the lime still. If any CO_2 has not been driven out in the heater liquor, this will carbonate the lime in the lime still, causing loss of available lime:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{15}$$

If any H_2S has not been completely driven out in the heater, some sulfide will be present in the distiller waste causing loss of sulfide.

$$Ca(OH)_2 + 2H_2S \rightarrow Ca(HS)_2 + 2H_2O \tag{16}$$

Hence the heater is a very important division of the distiller. It is not a difficult matter to drive out all fixed ammonia with a slight excess of lime and sufficient steam; but complete disappearance of CO_2 and also H_2S from the heater liquor before entering the lime still calls for a good design of heater, careful study of the arrangement, and good temperature control in the distiller.

The heat is introduced at the bottom of the lime still in the form of exhaust steam, generally 8-10 lb. gauge, and, when necessary, also some high pressure steam. To conserve the heat against radiation, the outside of the distiller and heater is lagged heavily with an insulating material.

The filter liquor leaving the filters has a temperature of 25°-30° C. It is heated up to 55° C. through the furnace gas scrubber and by the addition of various steam-ammonia condensates. The liquor preheater, on top of the heater, heats the liquor up further to about 75° C. before it enters the heater. The outgoing ammonia gas from the top of the liquor preheater entering the condenser is at 82°-86° C. The condenser cools the ammonia gas from 82°-86° C. down to 55°-60° C., so that there must be cooling surface in the partial condenser enough to take care of a temperature drop of about 30° C. Attempts to run the condenser at a temperature lower than this may cause crystallization of ammonium carbamate or carbonate in the condenser.

Distiller Waste—The excess lime in the bottom compartment of the lime still should be 2-3 g. CaO per liter. Therefore, there is a saving in lime if the liquor volume in the distiller is kept small. The composition of distiller waste is shown in Table 15:

TABLE 15—COMPOSITION OF DISTILLER WASTE

Sp. gr. at 15° C.	1.10-1.15
$CaCl_2$	90-95 g/l
NaCl	40-45 g/l
CaO	2-3 g/l
$CaCO_3$	6-15 g/l
$CaSO_4$	3-5 g/l
$Mg(OH)_2$	3-10 g/l
Fe_2O_3 and Al_2O_3	1-3 g/l
SiO_2	1-4 g/l
Total NH_3	0.006-0.012 g/l

The volume of the distiller waste liquor is about twice that of the brine used in the process. Larger plants with close regulation can keep this waste volume at or below 350 cu. ft. per ton of soda ash.

In 1½-2 months' time, scale formed in the overflow passages of the lime still, on the division plates and in the mushrooms becomes so thick that the liquor will not flow readily from one division plate to another below, and the distiller shows a tendency to fill up. Then it is time to change the distiller for cleaning. The period for cleaning varies a great deal in each individual works, depending upon the composition of limestone used, the composition of the feed liquor to be distilled, the conditions under which the lime still is operated, and the particular features of the lime-still construction. Table 16 shows a complete analysis of a hard scale formed in the lower portion of the lime still.

TABLE 16—COMPOSITION OF DISTILLER SCALE AT BOTTOM OF LIME STILL

	Per Cent
$CaSO_4$	62.41
CaO	30.32
$MgSO_4$	2.35
$MgCO_3$	1.62
Na_2SO_4	1.17
$NaCl$	1.65
Fe_2O_3	0.20
Al_2O_3	0.08
SiO_2	0.32
Moisture	0.60

Products from Distiller Waste—The analysis reported in Table 15 shows that the bulk of the solids in distiller waste is made up of chlorides. This arises from the fact that the waste contains all the chlorine from the salt used, because unlike the LeBlanc process, chlorine is not utilized in the process. Because of high cost of fuel required to concentrate such a weak liquor and because of limited demand for calcium chloride and the cheapness of this product, comparatively little of this distiller waste has been worked up, considering the very large volume turned out daily from the ammonia-soda industry and sent to waste.

The solid matter accumulates so fast that the disposal of this waste is a matter of no small concern to ammonia-soda manufacturers. Calcium chloride in solution permeates the soil bed and contaminates sources of water supply. Only to a very limited extent is any portion of the waste allowed by the municipal authorities to be sent to rivers or any public waterways, and that only after complete settling. Cases are on record where fish in the river were killed by the calcium chloride and the free lime carried in the liquor, so that ammonia-soda manufacturers are, in a way, obliged to do something with this waste. Proposals have been made to utilize it in many different ways, and various products claimed to have been prepared therefrom. Many of these are simply pure notions and have no practical value. The preparation of chlorine gas (for bleaching powder) or hydrochloric acid from calcium chloride in the waste must no longer be considered workable in view of the present more economical methods for preparing such materials.[17]

There is considerable unconverted salt in the waste. It must be said that the ammonia-soda process is very wasteful in the use of salt, the average efficiency of conversion of salt to sodium bicarbonate in the columns (or carbonating towers) being not more than 75 per cent in actual operation, so that, considering some additional losses in the form of "mud" in the settling vats, more than 25 per cent of the salt taken is wasted. As a result, the very existence of the ammonia-soda works presupposes a cheap and abundant supply of salt, and because of this fact it generally does not pay to recover this salt in the distiller waste. The salt so recovered, however, possesses a high degree of purity and may be com-

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[17] See Chapter 9.

parable to the product obtained from brine purified by soda-lime treatment. This salt is recovered in conjunction with the manufacture of calcium chloride.

We will discuss a few principal products that have been prepared from the distiller waste, on a commercial scale, namely, the refined salt, calcium chloride, calcium sulfate, and ammonium chloride.

Refined Salt and Calcium Chloride. It is the aim of the ammonia-soda operators to keep the volume of the distiller waste as small as possible, especially when any of it is to be worked up. This is done by keeping the volume of the filter liquor as small as possible, securing the highest decomposition possible in the columns; and by using as little wash water on the filters as is necessary to get the sodium chloride content in the ash within allowable limits; and by employing a strong milk of lime, containing 250 g. CaO per l. (sp. gr. 1.21), or using solid lime in the prelimer for the distilling operation. The liquor, which contains a small excess of free lime, is carbonated by passing some waste CO_2 gases through it. On settling, the precipitated $CaCO_3$ and all solid matter carried in the liquor, separate out. The clear solution containing $CaCl_2$, NaCl, and a small amount of dissolved $CaSO_4$, is concentrated in a triple effect evaporator, when NaCl, together with the little amount of $CaSO_4$, commences to crystallize out. The salt crystals are dried in centrifuges, a little water being sprayed on it to wash out calcium chloride from the salt. From the centrifuges the salt can be packed directly into barrels without further drying.

Evaporation is carried on until the specific gravity of the liquor in the last effect shows 42 Bé. At this point, practically all of the salt can be settled out. Some "chloride of lime" is added to oxidize the iron and the liquor then allowed to settle. The clarified liquor is further concentrated in cast iron pots until the molten mass solidifies on cooling, giving what is known as 75 per cent calcium chloride corresponding to the formula $CaCl_2 \cdot 2H_2O$. This product is ladled to steel drums, each containing about 600 lbs., and sealed. This product has a typical analysis shown in Table 17.

TABLE 17—COMPOSITION OF 75 PER CENT CALCIUM CHLORIDE

	Per Cent
$CaCl_2$	73.6
NaCl	1.4
Insoluble matter	0.08
Water	24.92

Anhydrous calcium chloride can be made by heating this 75 per cent $CaCl_2$ in a reverberatory or puddling furnace and frequently raking the molten mass, when some $CaCl_2$ is decomposed, giving CaO and HCl. The escape of this hydrogen chloride gas leaves a porous mass of fused calcium chloride which is known as 95 per cent $CaCl_2$. The cooled anhydrous mass, somewhat fluorescent, is packed in steel drums or paper-lined wooden barrels, hermetically sealed.

Calcium chloride solution is used as brine in the manufacture of ice, and as an anti-freezing solution; and the 75 per cent solid is used as a dust layer to minimize dust on public highways, while in the anhydrous form it is used as a catalyst to promote the reaction between calcium carbide [18] and nitrogen gas in the manufacture of calcium cyanamide, permitting a lower temperature to be employed.

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[18] See Chapter 8.

Calcium Sulfate. The crystalline $CaSO_4 \cdot 2H_2O$ is known as Crown Filter among the Solvay products. It is a much purer product than natural gypsum. The process of manufacture consists in settling the distiller waste and, while it is still hot, treating the settled liquor with salt cake. The excess of free lime carried in the liquor will be neutralized by the small excess of H_2SO_4 in the salt cake. If the resulting solution is slightly acid, some milk of lime may be added. The precipitated $CaSO_4 \cdot 2H_2O$ is filtered on a vacuum drum filter and further dried in a centrifuge, water being sprinkled on the crystals to wash away the soluble salt. The crystals of gypsum are dried at a reduced temperature much in the same way as the refined sodium bicarbonate. It is used as a paper filler.

When dried at or below 190° C. this gives plaster of Paris, $CaSO_4 \cdot \frac{1}{2}H_2O$, which is used for making molds, for wall plaster, and for many purposes in the building industry. When calcined at a temperature above 200° C., it loses all its water, care being taken that none of the sulfate is reduced to sulfide. When traces of iron are present, the calcined mass is discolored and shows a yellow tint. Calcined calcium sulfate is used in the manufacture of certain tooth pastes and in the manufacture of wall and flooring plasters.[19]

The filter liquor after removal of the precipitated calcium sulfate is a very pure brine which is sent to soda works for making saturated brine for soda manufacture.

Ammonium Chloride. Ammonium chloride is made from calcium chloride liquor obtained from the distiller waste by means of ammonia and CO_2 gas. For this purpose, the distiller waste is settled to eliminate solids, evaporated to about 40 Bé. in evaporators, to contain about 50 per cent $CaCl_2$. Salt separating out is filtered off and the calcium chloride liquor is placed in a tank provided with a stirrer, to which tank ammonia is first introduced and then the CO_2 gas. The temperature is allowed to rise to about 60° C. when $CaCO_3$ separates out in large crystals that are readily filtered and washed.

$$CaCl_2 + 2NH_4OH + CO_2 \rightarrow CaCO_3 + 2NH_4Cl + H_2O \qquad (17)$$

The filter liquor containing a high concentration of NH_4Cl is concentrated and cooled in large crystallizing pans where NH_4Cl separates out. The crystals are filtered in a centrifuge, slightly washed, and dried by means of hot air at a low temperature. Ammonium chloride so made contains only 0.3-0.4 per cent NaCl and is sufficiently pure for most commercial purposes.

EXTENT OF LIME USE

Because the bulk of the products from the ammonia-soda plants do not contain calcium, the public has but little idea of the extent of the use of lime in such plants.

Actually, the ammonia-soda industry is the largest single consumer of lime among all chemical industries; and the quantity consumed by this industry in the United States exceeds one third of the total output of lime in the country.

Take, for example, the year 1937 [20] when the quantity consumed by all chemi-

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[19] See Chapter 22.

[20] "Lime," Minerals Year Book 1938, Bureau of Mines, Dept. of the Interior, Washington, D. C.

cal industries other than the ammonia-soda industry totalled 2,151,444 short tons, distributed as shown in Table 18.

TABLE 18—QUANTITIES OF LIME CONSUMED IN INDUSTRIES OTHER THAN AMMONIA-SODA (IN U. S. A. 1937)

	Short Tons
Glass works	167,438
Metallurgy	694,814
Paper mills	447,728
Sugar refineries	21,211
Tanneries	61,544
Water purification	212,213
Other uses	546,496
Total	2,151,444

If we include lime used in building and agricultural work, the total for the year 1937 was 3,506,439 short tons, as shown in Table 19.

TABLE 19—CONSUMPTION OF LIME IN U. S. A. (1937)

	Short Tons
Building	948,533
Agriculture	406,462
Chemical industries other than ammonia-soda (as above)	2,151,444
Ammonia-soda (see below)	2,045,000
Total	5,551,439

In the same year this country produced—ammonia soda ash 2,205,006 short tons and caustic soda (by lime process) 488,807 short tons. Assuming an average figure of 1.25 tons of limestone required for the manufacture of 1 ton of soda ash, or 0.75 ton of lime as burned per ton of soda ash, the total lime consumed in the manufacture of ammonia soda is roughly 1,654,000 short tons. If we take roughly 0.80 ton of lime per ton of caustic made, 488,807 tons of lime caustic would require approximately 391,000 short tons of lime. Therefore, the total quantities of lime consumed by the ammonia-soda and lime caustic manufacturers for the year 1937 were 2,045,000 short tons and this quantity is considerably more than one-third of the total lime produced, as shown in Table 19.

From 1933 on, the ammonia-soda industry in this country has migrated southwards to the Gulf Coast, utilizing the great deposits of good rock salt in the form of domes or "plugs" and the oyster shells from the Gulf shore. One of three new ammonia-soda plants in Texas-Louisiana territories uses the oyster shells exclusively in place of regular limestone. These are found as reefs along the sea-coast near the mouths of streams which empty into the Gulf. These shells are dredged and washed before burning. The composition of these oyster shells is hardly distinguishable from that of a good-grade, low-magnesium limestone, except that they contain more organic matter. See Table 20.

These oyster shells are burnt in rotary kilns,[21] being too fine and too fragile to be charged with coke into the standard vertical shaft kilns.

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[21] For the operation of rotary kilns in lime burning see Chapter 22.

TABLE 20—COMPOSITION OF OYSTER SHELLS

	Per Cent
Calcium carbonate, $CaCO_3$	96.1
Magnesium carbonate, $MgCO_3$	1.3
Calcium sulfate, $CaSO_4$	0.36
Silica, SiO_2	1.3
Combined oxides, Al_2O_3, Fe_2O_3, etc.	0.33
Balance undetermined, organic matter, etc.	0.61

CAUSTIC SODA

Caustic soda is one of the very important chemical commodities. Great quantities are used in the manufacture of such commodities as rayon, soap, paper, mercerized cotton, explosives, dyestuffs, etc.[22] Although the electrolysis of brine[23] now supplies a very large proportion of the caustic soda there are certain advantages in manufacturing it in conjunction with the ammonia-soda process. First, in conjunction with the manufacture of sodium bicarbonate, which requires an excess of CO_2 gas from the lime kiln, the corresponding excess of CaO obtained is best utilized in causticization; second, ammonia soda makes a highly pure soda ash as raw material for caustic soda manufacture, yielding a product often higher in purity than the electrolytic caustic; and third, unlike the electrolytic caustic industry, it has no joint product such as bleaching powder or liquid chlorine to complicate the manufacture. On the other hand, recent rapid increases in the demand for chlorine[24] have given impetus to the use of the electrolytic process.

The method of causticization is a well-known one:

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$$

The reaction depends upon the small solubility product of Ca^{++} and CO_3^{--} ions, causing precipitation of solid $CaCO_3$. As both Na_2CO_3 and NaOH are very soluble, the reaction depends upon the solubility of $CaCO_3$ relative to that of $Ca(OH)_2$. As the reaction proceeds, the concentration of NaOH increases and that, by common ion effect, greatly decreases the solubility of $Ca(OH)_2$ until ultimately it is no more soluble than $CaCO_3$, when the following equilibrium is set up:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$

Hence, conversion of Na_2CO_3 to NaOH cannot proceed to completion. Examining the mathematical expression of equilibrium,[25] one can see that the more dilute the soda solution, the higher will this conversion percentage be. With 10 per cent soda solution, for instance, the theoretical conversion is 97 per cent, but in practice, using a 1.17 sp. gr. liquor containing 16 per cent Na_2CO_3, the conversion ratio is not over 91-92 per cent. Too dilute a liquor requires an excessive

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[22] See Chapters 38, 42, 37, 32, 28.

[23] See p. 438.

[24] For further discussion of this particular inter-process competition, see Chapter 2.

[25] Hou, T. P., "Manufacture of Soda," A. C. S. Monograph No. 65, Chapter XIX, "Manufacture of Caustic Soda—Chemical Process," Reinhold Publishing Corp., New York, Second Edition (1942).

amount of fuel for concentration; hence a close study must be made between the degree of conversion obtainable and the cost of fuel.

Batch Process—The soda solution from storage tanks is causticized in large tanks, 10-14 ft. in diameter, 8-9 ft. deep, with a flat bottom. Steam is used to heat up the liquor to 190°-200° F. and a compressed-air line can be provided for agitating. The tanks are each provided with a mechanical stirrer having a set of bevel gears driven by a pulley from a counter-shaft. Lime in lumps of 6-in. size or smaller is added to the steel basket attached to the side and partially submerged in the liquor, in an approximate ratio of 60 lbs. lime to every 100 lbs. of Na_2CO_3 in solution. The basket is perforated, bottom and sides, with ½-in. holes. When closer control is desired, instead of solid lumps, milk of lime having a concentration of about 250 g. CaO per l. is used. Several such tanks can be used in rotation, one operating while the others are settling and washing. Decantation of the supernatant caustic solution is done through a swing pipe with outlet attached to the side near the bottom of the tank.

After sufficient lime has been added and the desired conversion per cent obtained, as shown by a titration with double indicators, the liquor is allowed to settle for about 2 hours. The clear portion is drawn off through the swing pipe and this gives a strong lye for evaporation. The lime sludge, with what lye remains, is washed with the third liquor from a previous batch, the stirrer is started, and the liquor is heated with steam. After settling, this gives the second liquor of 7°-8° Bé., which may be added to the lye tank. The slime is again washed with the fourth liquor in a similar way and this gives the third liquor, which is used for second washing and also for making soda solution for causticization. Finally, the slime is further washed with fresh water, giving the fourth liquor, mentioned above. This washed slime, containing the precipitated $CaCO_3$, with the little alkali that remains, is washed out and sent to waste. A causticization batch can be made in every 2½ to 3 hours, but this, coupled with the time for washing, settling and decanting, makes the cycle for each tank about 16 hours.

Continuous Process—A more recent development is the addition of soda ash into milk of lime in a mixing trough in definite proportions. The mixture then flows into the causticizing tank. This permits accurate control, since the flow of milk of lime can be measured through an orifice tank, and the rate of soda ash added can be controlled by a mechanical feeder. Thus, the feed into the causticizer and the discharge overflowing from the causticizer can both be made continuous. Then the settling of the causticized liquor, washing of the sludge, and transferring of the different wash liquors from one settling tank to the other may be strictly made continuous and counter-current.

A more efficient apparatus of this type which gives more thorough washing with less water is the Dorr thickener[26] which permits continuous settling and decanting. Washing is done in the same type of apparatus in a strictly counter-current way. Thus when three thickeners are used in series, the lye from the agitators, or causticizing tanks, is drawn to the first thickener, the overflow from which is sent to the evaporators for concentration. From the bottom of the first thickener the sludge is pumped to the second thickener by means of a diaphragm pump, in which it is washed with the overflow from the third thickener. The

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[26] See Chapter 2

overflow from the second thickener goes to make soda solution for causticizing. The sludge from the second thickener is similarly pumped to the third thickener, in which fresh water is used for washing and from which the sludge is filtered on a rotary vacuum filter and the cake washed with fresh water and sent to waste, or burnt in a small rotary kiln for the recovery of lime. In this way, comparatively small floor space is required and the recovery of alkali is as high as 99.7 per cent. The upkeep is low and the power consumed very small.

Evaporation—The lye from the finished liquor tanks is concentrated in multiple effect evaporators, generally having three effects, using backward flow feed.[27] The most common types of evaporators for caustic liquor are those of the Zaremba, Swenson, and Buffalo Foundry, using exhaust steam. The concentration of caustic liquor in the last effect is brought to 47 Bé. and the liquor is then drawn out to tall settling tanks in which salt and soda separate out, these two being sparingly soluble in caustic solution at this concentration. Often a single effect using high pressure steam (as much as 75 lbs. per sq. in. gauge) and fitted with pure nickel tubes, is employed for concentrating the caustic from the third effect in order to bring the final concentration to 65 per cent NaOH or higher.

The liquor is settled by cooling, and the clarified caustic is drawn to a number of open cast-iron pots, 10 ft. or more in diameter, 4 to 5 ft. deep, and 2 ins. in thickness of the shell. The pots are heated by direct fire and the temperature is gradually raised until it reaches about 500° C., when the molten mass is quietly boiling. At this point a dark scum of graphite may be seen. The iron oxidizes to Fe_2O_3, which settles to the bottom. Just before settling, a small amount of flowers of sulfur is thrown over the surface of the molten mass to "bleach" the caustic so that, after solidification, it shows white color. The contents of the pot are allowed to settle and the molten mass is pumped or ladled out into steel drums, each holding about 675 lbs. The mass solidifies on cooling and the drum is immediately sealed to prevent absorption of moisture. This gives the commercial 76 per cent Caustic (76 per cent Na_2O) containing 98 per cent NaOH. The chemical analysis is given in Table 21.

TABLE 21—COMPOSITION OF SOLID CAUSTIC

	Per Cent
NaOH	98.0
Na_2CO_3	1.2
NaCl	0.2
Na_2SO_4	0.06

As there is no sulfide or thiosulfate in the ammonia-soda liquor, no nitre need be added to the pots. The caustic "bottom" in the pots contains much Fe_2O_3 and is of reddish yellow color. It is redissolved and the Fe_2O_3 separated out by settling, the clear liquor being returned to the evaporators for concentration.

Liquid Caustic—Strong caustic liquor from the last effect of the evaporators giving 47 Bé. (or about 45 per cent NaOH) after complete settling is sold as liquid caustic. It is usually shipped in rubber-lined steel tank cars provided with steam coils for thawing in winter and is used in many industries (rayon,

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[27] See Chapter 2.

soap, etc.). Liquid caustic in commerce may be either 50 per cent or 74 per cent NaOH. The rayon industry requires extra-refined caustic which must contain only small amounts of iron, copper, and aluminum, and traces of silica. The requirements are so stringent that nickel or nickel-clad equipment and tanks are employed in its manufacture and extreme care is exercised not to introduce such impurities into caustic liquor in the process of manufacture.

MISCELLANEOUS PRODUCTS

Besides the principal products described above, the ammonia-soda plants usually manufacture several miscellaneous items which might be classed as by-products.

Sodium Bicarbonate—Sodium bicarbonate, commercially known as bicarbonate of soda, is a product directly related to the ammonia-soda industry. At first thought it would seem natural to start with the crude bicarbonate from the filters and refine it. There are, indeed, many patents taken out dealing with refining this bicarbonate by redissolving and recrystallization. Such methods are not used in practice. On account of the presence of ammonia, which amounts to 0.7 to 0.8 per cent NH_3 and which must be recovered, such methods can not be simply carried out. The ammonia-soda manufacturers prefer to make it from soda ash, or partially decomposed crude sodium bicarbonate by "wet" calcination. This seems to be a roundabout way, but after all it is simple and lends itself well to practical operation, because:

1. There are no ammonia losses to contend with.
2. CO_2 gas is recovered in a rich form while lean gas can be used for recarbonating.
3. About the same apparatus can be used in settling, carbonating, filtering, etc., as in soda ash manufacture. In fact, some of the antiquated apparatus from soda works may be utilized in its manufacture.

The process consists in dissolving soda ash to make a saturated solution, for which purpose a tank dissolver provided with a stirrer, or better still, a rotary dissolver, can be used. The solution is settled in a series of settling vats (generally three) and after passing through coolers, it flows by gravity to a storage tank, from which it is pumped to the recarbonating tower which is much the same as that used in soda manufacture, but perhaps having less cooling surface. The gas is sent in by CO_2 compressors as usual. The draw temperature is higher, about 39° C. The crystals are filtered and washed, first on a rotary drum filter as in soda ash manufacture, and then in centrifuges much the same as those employed in a sugar refinery. These centrifuges reduce the moisture left in the bicarbonate to about 8 per cent. The filter liquor is used over again in making soda solution. When this filter liquor gets too concentrated in NaCl through repeated use, it is sent to the soda ash plant for making saturated brine. Fresh soft water is then added for replenishment. At intervals of 4 to 5 days, the tower gets dirty and needs cleaning, which is done by filling the tower with water and boiling out with steam. The boil water is drawn out and, after settling, stored in feed liquor tanks for making soda solution. No sulfide is introduced to the soda solution for recarbonating.

The bicarbonate from the centrifuges is dried either on a continuous belt conveyor consisting of a number of conveyor sections enclosed in a chamber, with a steam heater at the entrance end (to heat the incoming air) and an exhaust fan at the other end to pull the hot air through (Figure 6); or better still, in a vertical tube, some 50 ft. high and 24 ins. inside diameter (Figure 7).[28] The bicarbonate from the centrifuge is charged in through the feed table midway up and is blown up by hot air from a centrifugal blower at the bottom of the tube. The bicarbonate particles suspended in the hot blast are dried as they reach the top, where two large cyclones in series are attached to the outlet of the tube to receive the dried bicarbonate. The exhaust from the second, and generally larger, cyclone, containing some extra light particles, is led into a large dust-collecting chamber on its way to the atmosphere. This dust-collecting chamber is built of wooden frames on all sides, covered with cheesecloth. The temperature of the hot air is maintained at 70°-90° C. and the blast from the centrifugal blower at 10 ins. H_2O. From the cyclones the bicarbonate is conveyed in screw conveyors to a packing bin, from which it is packed into barrels varying in size from 350-550 lbs. and sometimes also in small kegs of 112 lbs.

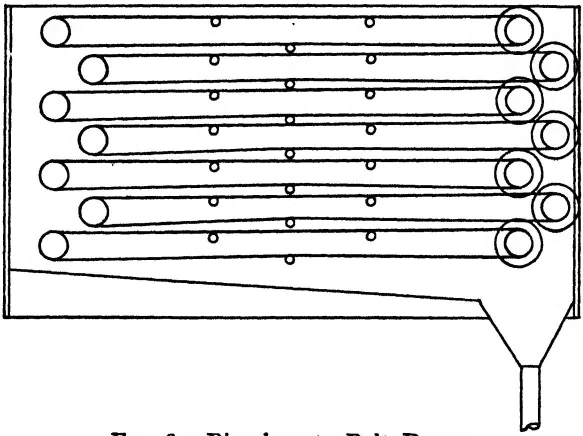

FIG. 6. Bicarbonate Belt Dryer.

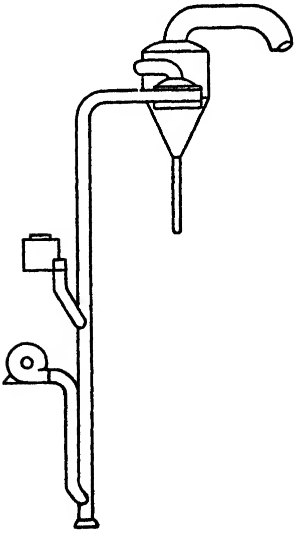

FIG. 7. Vertical Tube Dryer.

The bicarbonate so manufactured has a remarkably high degree of purity as shown in Table 22. This can be understood when we remember that it is made from ammonia-soda ash having, to start with, 99+ per cent Na_2CO_3 and 0.4-0.5 per cent NaCl.

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[28] Hou, T. P., "Manufacture of Soda," A. C. S. Monograph No. 65, Chapter XVIII, second edition, Reinhold Publishing Corp., New York (1942).

Sodium bicarbonate is used for making baking powder, carbonated waters, and in fire extinguishers, and in the manufacture of leather, drugs, and chemicals.

TABLE 22—COMPOSITION OF REFINED BICARBONATE

	Per Cent
$NaHCO_3$	99.70-99.85
NaCl	0.10- 0.15
Fe_2O_3	Trace

Sal Soda—Sal soda, washing soda, or soda crystals, is the decahydrate of sodium carbonate, $Na_2CO_3 \cdot 10H_2O$. The crystals are formed from a solution at a temperature below 35° C. In the old days when pure soda could not be obtained from the LeBlanc process, people preferred to use soda crystals in order to avoid having caustic and to insure getting a purer product. It is used in washing and in the scouring of wool. Nowadays a very pure soda ash can be obtained from the ammonia process and the trade in sal soda is declining on account of its freight cost and the difficulty of keeping the crystals in shape.

Its manufacture requires a large floor space. When the solution is prepared from ammonia-soda ash, a tank provided with a stirrer much like the causticizing tank is used. Water is heated to about 100° F., i.e., to the point of maximum solubility, and soda ash, together with the desired amount of sodium sulfate, added until its sp. gr. shows 36 Bé. at this temperature. This requires about 50 per cent soda ash. After all has been dissolved, the stirrer is stopped, the solution allowed to settle, and the clear portion drawn to crystallizing pans. These are 10 ft. wide by 10 ft. long by 2 ft. deep from the top to the pyramid bottom. The pans are set on brick or concrete piers, so that the mother liquor can be drawn from the bottom. They are set aside to crystallize for 7 to 10 days, depending upon the size of the pan, the weather conditions, etc. In hot summer days this operation is attended with difficulty. Galvanized-iron wire netting is suspended across the pans just under the surface of the liquor. Crystals are formed hanging from these wires immersed in the liquor. After crystallization, the mother liquor shows a Bé. reading of 20°-22° and is drawn off for making the soda solution again. The crop of crystals formed on the sides and bottom are chiseled off and charged to centrifuges to whirl out the enclosed mother liquor. The crystals are packed in wooden barrels each containing 280 lbs.

Instead of the dissolving tanks described above, a small rotary dissolver with angle iron flights riveted on the shell inside gives a continuous operation and has a very large capacity, the solution being settled in a separate tank outside.

The manufacture of sal soda possesses some advantage in that discolored soda ash and floor sweepings can be dissolved and utilized for its manufacture. Thousands of tons of red soda produced when first starting up a new plant, have been utilized in this way or in the manufacture of caustic soda.

In order to obtain better crystals from ammonia soda, anhydrous sodium sulfate is added with the soda ash to the extent of 3 to 5 per cent by weight. This, of course, contaminates the product but the users generally do not object to it.

Both soda ash and sodium sulfate possess maximum points of solubility corresponding to transition points from one hydrate to another. This is about

35° C. for soda ash and 33° C. for sodium sulfate. Hence the temperature for dissolving is best kept around 35° C.

Sodium Sesquicarbonate—This product, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, is known as Concentrated Crystal Soda in England but as Snow Flake Crystals among Solvay products in America. In natural form it is known as "trona." It consists of fine, lustrous, needle-like crystals. It is a stable compound, neither hygroscopic like soda ash nor efflorescent like sal soda, and so does not form lumps on storing. It is readily soluble in water and dissolves without evolution of heat, like Na_2CO_3 or $Na_2CO_3 \cdot H_2O$, nor absorption of heat, like $Na_2CO_3 \cdot 10H_2O$. This compound exists to a large extent in natural soda deposits.

The crystals can be manufactured by adding an excess of sodium bicarbonate to a hot soda ash solution in the ratio of slightly over 84 parts $NaHCO_3$ to 53 parts soda ash, by weight. The resulting strong solution is allowed to cool slowly to about 35° C. when fine, shiny crystals will be formed.

There is a process of making refined sodium bicarbonate from the filtered crude bicarbonate by dissolving the latter hot, distilling the solution as in the distiller operation but without the addition of lime, settling the solution, cooling, and finally recarbonating the cooled, settled liquor as in the carbonating tower operation. During distillation, a considerable amount of the bicarbonate is decomposed to normal carbonate, and instead of recarbonating it, a portion may be employed for the manufacture of the sesquicarbonate by concentrating and cooling. The crystals are dried at a reduced temperature and packed in barrels containing 280 lbs. The sesquicarbonate, being stable, rather neutral, and readily soluble, finds much favor in wool scouring and in laundering.

Crystal Carbonate—This is the monohydrate of soda ash and is obtained by crystallization from solution like sal soda, but a very much higher temperature. Theoretically, a temperature above 35° C. will yield these crystals: in practice, boiling temperature is employed because of the ease with which the solution is concentrated. This is a rather stable compound to which sal soda is converted on exposure, in the form of fine white powder. Natural soda deposits give this white powder on the surface layer by efflorescence. By absorption of CO_2 and moisture from air, crystal carbonate, $Na_2CO_3 \cdot H_2O$, forms the sesquicarbonate, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. Much of the monohydrate is also obtained from the double salt burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) at the American Potash & Chemical Corporation's plant at Trona, Searles Lake, California.[29]

Modified Sodas—Various mechanical mixtures of sodium bicarbonate and soda ash containing from 25 to 75 per cent bicarbonate by weight are put up under the name of modified sodas to meet certain demands in the market. The "Tanners' Soda" is one of such sodas. They are used where a milder alkali is preferable.

Causticized Ash—Various mechanical mixtures of caustic soda and soda ash containing from 10 to 50 per cent caustic are put up to meet requirements in certain industries like bottle washing, metal cleaning, water softening, etc., where a stronger alkali is preferable.

Granular Ash—This is a coarse-grained dense soda ash made by using a rather high percentage of water. The granules are screened to specified sizes. Its

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[29] See Chapter 9.

dustless property is much favored by the glass industry. The dense ash is screened to give uniform size.

Block Soda—In the Orient, much soda is handled in block form. Large quantities of soda ash are made into blocks and sold in this form. This comes from the practice by which natural soda was handled in olden days. Soda ash in powder form has a tendency to "set" in contact with water when the mass is not disturbed by stirring and it will further unite with a considerable amount of water, maintaining its firm, solid form when cooled. When soda ash in a finely divided state has not absorbed any moisture by long exposure, a suspension, or thin paste, formed by stirring the fine powder into as much as 130 per cent of its weight of water will "set" to a firm, solid form on standing. The amount of water soda will take in this way depends upon (1) per cent Na_2CO_3 (not as $NaHCO_3$) in the ash, (2) the fineness of the powder, and (3) the weather conditions. The power of absorbing water and forming a firm, solid block is materially impaired if soda ash has in part been converted to $NaHCO_3$ or has absorbed moisture from air through long storage or during transportation over a long distance. To make these blocks, soda ash is screened and the coarser particles and lumps are pulverized until all pass through at least a 20-mesh screen. The powder is gradually stirred into 100 to 130 per cent of its weight of water at about 30° C. and the mixture continually stirred. The stirring operation is very important and serves to mix the ash thoroughly with water. As it is stirred, the mixture gradually thickens. Stirring is kept on until it has thickened to a consistency of a starch paste, when it is transferred to wooden molds, 34 ins. long by 14 ins. wide by 8 ins. deep, inside dimensions, and allowed to "set" for 24 to 36 hours, after which the blocks formed can be taken out by loosening the sides of the molds.

Some sodium bicarbonate is added to the paste towards the end of stirring, especially in the summer time. This serves to hasten the "setting" time, apparently by seeding action. It also gives a finer grain in the block. The amount of sodium bicarbonate required is 2 to 2½ per cent in winter and 3 to 5 per cent in summer, on the weight of soda ash taken. The blocks will thus analyze less than 50 per cent Na_2CO_3, and one typical analysis is given in Table 23.

TABLE 23—COMPOSITION OF BLOCK SODA

	Per Cent
Na_2CO_3	46.12
$NaHCO_3$	2.90
NaCl	0.56
Insoluble matter	0.33
Water	50.07

In the East, soda in this form, or in the decahydrate form, is used in making steamed bread, noodles, cakes, fryings, etc., and also in washing.

Ammonium Bicarbonate—Ammonium bicarbonate is made by passing CO_2 gas into aqua ammonia in an apparatus somewhat like the carbonating column, only much smaller. For this purpose one plant uses 26 Bé. aqua ammonia which has been redistilled in order to eliminate H_2S, etc., and then passes lean CO_2 gas into it. NH_4HCO_3 crystals are precipitated in the small column much in the same way as $NaHCO_3$, but the liquor contains a much higher concentration of

NH_3 than the ammoniated brine. The crystals are also somewhat coarser than the sodium bicarbonate crystals and are filtered in an open wooden box filter having a false bottom. The crystals are dried on a system of belt conveyors by means of hot air heated to a temperature of about 50° C., and packed in paper-lined wooden kegs or in small paper boxes. Ammonium bicarbonate is used to a limited extent in medicine, but in larger quantities as baking powder which yields carbon dioxide and ammonia gases to leaven the dough without leaving any mineral residue in the bread as do the other kinds of baking powder, although some people object to the slight odor of ammonia during baking. Ammonium bicarbonate has a high vapor tension and must be packed in closed containers kept in cool places. A process of getting a special form of crystals of ammonium bicarbonate having a very low vapor tension has been worked out so that the crystals could be packed in burlap bags in the same way as ammonium sulfate.

ELECTROLYTIC CAUSTIC AND CHLORINE

As early as 1800 the electrolytic method of caustic soda production was known, but it was not until about 1885 that successful commercial application was accomplished. Undoubtedly the perfection of the direct-current generator, or dynamo, contributed much to the success of the process. During the last several decades, it has become an important method for the manufacture of caustic soda, chlorine, and chlorine products. Caustic soda produced by the process has become a product of standard purity in the chemical trade. Wherever electric current can be cheaply generated, either because of the cheapness of coal or because of the presence of abundant water power, this electrolytic method has found a wide application. This is notably true at Niagara Falls.

In the United States, cells of diaphragm type are most commonly used for the electrolysis. The commoner ones are the Allen-Moore, Vorce, and Hooker cells. In what follows we shall describe the process in considerable detail, using the Allen-Moore cell, which is widely used in the paper and pulp mills throughout the United States, as an example of the rectangular cells; the Vorce cell as an example of the cylindrical cells; the Hooker S type cell as an example of cubical cells; and the mercury cell of the Castner type, a modified form of which is rapidly coming into use in this country.

Preparation of Brine—The brine to be used for electrolysis may come directly from wells. In this case it must be purified[80] before it is sent to the cells.

If the starting material is solid rock salt, the brine is prepared in a saturator; a tall, square concrete tank about 6 ft. square × 20 to 25 ft. high. The tank is kept full of salt. Water is introduced from the bottom of the tank, and the flow is so regulated that as it forces its way up it becomes saturated and flows from the outlet at the top as saturated brine. Salt is constantly added to keep the tank full, and the mud that accumulated in the saturator may be flushed out at intervals through the outlet opening at the bottom. The brine overflowing from the saturator should contain about 315 gm. NaCl per liter at a specific gravity of 1.20 at 25° C. Soft water, preferably warm, such as condensate or caustic wash water, is most desirable.

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[80] See Chapter 9.

Salt suitable for this purpose must be free from calcium, magnesium, and iron, and the brine made may be purified by chemical treatment before use; otherwise the diaphragms are liable to be clogged by the precipitated calcium and magnesium hydroxides in the cathodic liquor. This would cause short life of the cells. It is clear that, for this purpose, rock salt will be superior to sea salt obtained by solar evaporation. Good rock salt suitable for electrolysis should have the analysis given in Table 24.

TABLE 24—ANALYSIS OF ROCK SALT SUITABLE FOR ELECTROLYSIS

	Per Cent
NaCl	98.5
Insoluble matter	0.57
Moisture	0.07
CaO	0.28
MgO	Trace
SO_3	0.12
Fe_2O_3	Trace

The brine from the saturator flows to concrete storage tanks or asphalt-lined steel storage tanks from which it is pumped, or flows by gravity, to the purifying tanks. These are asphalt-lined steel tanks about 12 ft. in dia. by 10 ft. high. The method of purification is essentially the same as that employed for purifying brine pumped directly from wells.[30]

As the brine leaves the purification tanks, it is filtered through a sand filter which is a wooden tank having a false bottom. This false bottom is covered with burlap, over which is placed a 4-in. layer of coarse cinders, then a 2-in. layer of fine cinders, and finally a 4-in. to 6-in. layer of clean, coarse sand. Mud collects on top of the sand and the clear brine flows to acid-proof storage tanks. To prevent clogging of the filter, the sand should be back-washed at intervals; the schedule for cleaning must be determined by the individual condition of the plants. To save labor, the treated brine may be filtered through filter presses, such as made by Sweetland and other manufacturers.

To correct the alkalinity in the treated brine, commercial hydrochloric acid is added in slight excess (about 3½ lbs. commercial HCl to every 1000 gals. of brine) and the solution is agitated by compressed air. This acid reaction is also necessary in order to prevent any hypochlorite formation in the anode compartment during electrolysis. From these tanks the acidified brine flows to a constant level tank, thence to the individual cells through a feed control system. This treated and acidified brine has the composition shown in Table 25.

TABLE 25—ANALYSIS OF TREATED AND ACIDIFIED BRINE

Sp. gr. at 20° C.	1.196
NaCl	315 g/l
HCl	0.16 g/l
Na_2SO_4	2.0 g/l
CaO	0.67 g/l
MgO	Nil

Sea salt can be used, although the crystals contain more magnesium impurities. With soda-lime pretreatment, such impurities in the sea salt may be eliminated to within allowable limits in the brine.

Electrolysis of Brine—The essential reactions in the electrolysis of a cell where a permeable diaphragm separates the anode from the cathode are as follows:[31]

$$\begin{aligned} NaCl &\rightarrow Na^+ + Cl^- \\ 2Na^+ + 2\ominus + 2H_2O &\rightarrow 2NaOH + H_2 \qquad \text{(cathode)} \\ 2Cl^- + 2\oplus &\rightarrow Cl_2 \qquad \text{(anode)} \end{aligned} \tag{18}$$

Apart from secondary reactions, hydrogen gas is evolved at the cathode where NaOH is formed, while chlorine gas is given off at the anode. The sodium ions pass through the diaphragm and are electrolyzed to free sodium which immediately combines with water to give NaOH and H_2 as shown in the second reaction above. If OH^- ions migrate back to the anode the following reaction occurs:

$$2OH^- + 2\oplus \rightarrow H_2O + \tfrac{1}{2}O_2 \tag{19}$$

If cells using graphite anodes are used, oxygen so liberated oxidizes the graphite. This is also true when much sulfate is present, as $SO_4^=$ ions would carry current to the anodes liberating oxygen which attacks the graphite, cutting down the life of the anodes. This would cause loss of current as far as chlorine and caustic soda production is concerned. In order to prevent these excessive losses caused by the high OH^- concentration when graphite anodes are used, electrolysis is stopped when less than one-half of the total NaCl in the brine has been converted to NaOH.

Since chlorine gas is somewhat soluble in brine, if it for any reason comes in contact with NaOH, either hypochlorite or chlorate will be formed, according to the temperature conditions, as follows:

$$2NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O \text{ in the cold} \tag{20}$$

but

$$6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O \text{ in the hot}$$

Either HClO or $HClO_3$ will attack graphite anodes, producing CO_2, so that a small amount of Na_2CO_3 may be found with the caustic in the cell effluent

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \tag{21}$$

The theoretical voltage required can be roughly calculated from the following thermo-chemical equation, although the result is not accurate thermodynamically:[32]

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2 + Q$$

Here,

Heat of formation of 2NaCl in aqueous solution $= 2 \times 96{,}600$ cal.
Heat of formation of 2NaOH in aqueous solution $= 2 \times 112{,}450$ cal.
Heat of formation of $2H_2O$ in liquid state $= 2 \times 69{,}000$ cal.

$$\therefore Q = 2 \times -53{,}150 \text{ cal.}$$

$$V = \frac{2 \times 53{,}150 \times 4.187}{2 \times 96{,}540} = 2.3 \text{ volts}$$

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[31] The reaction in cells where there is no separating diaphragm, produces chlorates. See Chapter 11.

[32] For the correct theoretical cell voltage see Lewis, G. N., and Randall, M., "Thermodynamics," McGraw-Hill (1923).

This is the theoretical minimum voltage. Some energy is dissipated as heat through the resistance of the electrolyte. To minimize such losses, i.e., to secure the highest energy efficiency, the resistance through the electrolyte is reduced by placing the anodes as near to the cathode as possible; by having the electrode surfaces as large as possible; and by running the electrolyte rather hot.

Allen-Moore Cells—The present KML type cell is the improved Allen-Moore cell which was developed by Edward A. Allen and Hugh K. Moore at Rumford, Maine, as far back as 1895. (See Figure 8.) The original Allen-Moore cell was the first of its kind employed in an electrolytic chlorine plant in the United States.

To illustrate one typical installation, the following arrangement may be described. A 340 KW dynamo driven by a steam engine, Diesel engine, or A. C. motor, having a terminal voltage of 230 v. feeds the current through 64 such cells connected in series and arranged in two rows along each side of the room. At present, large electrolytic plants also use mercury arc rectifiers which have good economy in D. C. generation, especially where the total voltage required is 440 v. or higher. The bus-bars connecting the anodes or graphite electrodes are copper bars of varying cross section, which are connected to each graphite electrode by means of a copper lead. There are 24 of such graphite anodes arranged in two rows with 12 on each side. These anodes are placed close to the perforated iron sheet cathode and are separated by asbestos sheets which serve as the diaphragm supported by the cathode. The gap between the cathode and the anode surface is only about ½″ and the lower ends of the graphite anodes are kept separated from the cathode, and from each other, by means of porcelain spacers. From the anodes, the current travels through the brine and through the asbestos diaphragm supported by the cathode which in the newer type is W-shaped. From the cathode the current is collected by another bus-bar which delivers it to the graphite anodes of the cell next in series, and so on. Enclosing the per-

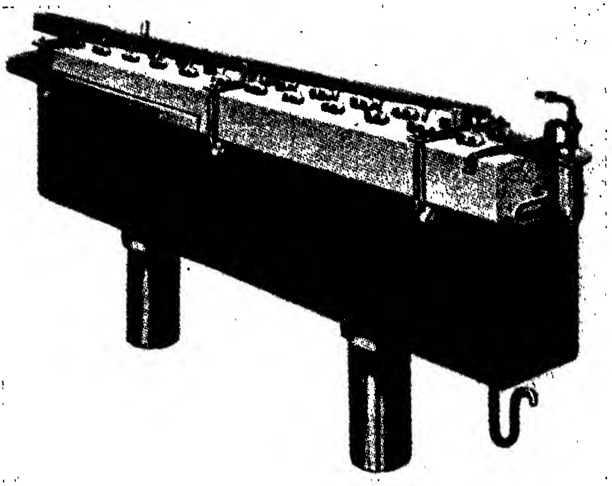

Fig. 8. Type KML Allen-Moore Cell. [Courtesy Electron Chemical Co. (Allen Electrolytic Cell Corp.)]

forated iron sheet and the asbestos diaphragm is a space or cathode chamber in which the electrolyzed brine collects and drains out of the cell from the bottom through a U-loop seal. The cathode chamber consists of a steel tank carrying a half-inch pipe for the outlet of the effluent at the bottom, and a vent pipe for the exit of the hydrogen gas. (See cross-section view, Figure 9.)

The anode chamber, which is set on the top of the steel tank, is constructed of carefully deposited concrete, consisting of 1 part cement to 3 parts clean stone or quartz pebble crushed to ½-in. size. The inside surface of the concrete is painted with a coal-tar protective paint. The chlorine outlet is located on the top of the concrete anode chamber. The anodes consist of individual Acheson graphite boards, 1¼″ thick × 30″ long × 6″-8″ wide. Joints, if any, are carefully machined and fitted to one another to minimize voltage drops. These graphite anodes last about 12 to 18 months while the asbestos diaphragms last from 12 to 18 weeks.

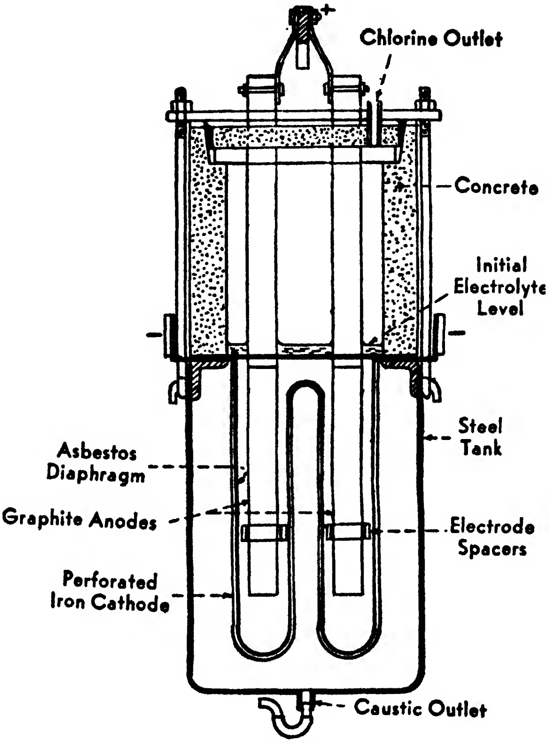

Fig. 9. Allen-Moore KML Alkali-Chlorine Cell in Cross Section.

Each cell has an overall length 8 ft.-6 in., width 1 ft.-2½ in., and height 3 ft., weighing approximately 1330 lbs. The height of the pier and insulator is 1 ft.-5 in. To cut out a cell, the current is short-circuited by clamping a copper bar onto the anode bus-bar on the cell to be cut out and connecting it to the anode bus-bar of the next cell.

Operation of the Cells. The brine level is maintained constant by means of a special float control located at one end of the cell. Brine is fed from a cast-iron header to the anode compartment from a head tank, the header being provided with a tee for each cell, connected by a union to a nipple next to the rubber valve which carries a flexible rubber tubing for delivering brine to each cell. The weak liquor, or cell effluent, from each cell is drained continuously into a concrete trough, running to weak liquor storage tanks.

Hydrogen gas is let out into the room through vent pipes, on top of the cathode chamber, or else is collected and compressed into steel cylinders at 120 atmospheres pressure. In several plants, hydrogen gas produced this way has been utilized for the hydrogenation of oils. With the development of synthetic ammonia process for the manufacture of ammonia, hydrogen gas has formed an important raw material for direct union with nitrogen. Also, it may be burned with chlorine gas for the manufacture of hydrochloric acid. Chlorine gas is collected through a stoneware pipe located on top of the anode compartment, and is drawn by means of a stoneware or hard lead exhauster through the absorption towers when bleach is to be made. The top of the anode chamber is covered with concrete and the whole is luted over with coal-tar cement to prevent leakage of air into, or of chlorine gas out of, the anode chamber.

The voltage across each cell is taken once a day and the cell effluent tested for strength of caustic and the presence of hypochlorite. Anode gases are tested by an Orsat apparatus to determine electrical efficiencies. Systematic records are kept of each cell. The voltage is maintained at about 3.5 volts per cell. The asbestos diaphragms gradually become clogged by solid deposits from calcium and magnesium hydroxides in the electrolyte, whereby the resistance to the flow is increased. To maintain the flow constant, therefore, it is necessary to raise the float and run a higher static head of the electrolyte on the diaphragm. With new diaphragms in a cell newly cut in, the rate of flow may be momentarily as high as 35 l. per hour, but in the course of time it gradually diminishes to about 20 l. per hr. Efficiency tests show that with a total current of 1500 amp. passing through the cells, the volume of effluent from each cell should be from 20 to 22 l. per hr. At the end of 18 weeks or so, the asbestos diaphragm may get choked so badly that proper flow cannot be maintained with the brine level at the highest point. It is therefore necessary to cut the cell out, renew the asbestos diaphragm, and clean the iron sheet cathode. A new diaphragm is made with three layers of asbestos paper for the bottom half and two layers for the top half. After a cell has been cleaned and assembled with a new diaphragm, the brine is fed in.

When the electrolyte has reached the top of the cathode chamber and normal flow has been reached, then and only then should the cell be cut in. At first, when the cell is cold, the resistance is high and the voltage drop across the cell will be temporarily excessive. But as the cell is gradually warmed up, this voltage will drop to 3.3 volts and then rise gradually to 3.5 volts. On the other hand, the new asbestos diaphragm being open, the flow for the time being may be high, causing an excessive amount of unconverted salt in the cell effluent. As the diaphragm gradually gets clogged up, however, the flow diminishes. After three or four months of continuous running it may fall below 16 l. per hour. It is then time to change the asbestos diaphragm, as the reduced rate of flow causes the formation of much hypochlorite in the anodic liquor and reduces the current efficiency. Oftentimes the addition of some hydrochloric acid to the feed will prevent the formation of hypochlorite.

The current density employed in these cells is about 0.4 amp. per sq. in. The current efficiency is 93-94 per cent, while the overall power efficiency is about 62 per cent. The decomposition efficiency of NaCl is less than 50 per cent. The temperature of the cell liquor is about 43° C.

Some of the typical operating results of these cells are given in Table 26.

TABLE 26—SOME TYPICAL OPERATING DATA OF ALLEN-MOORE CELLS

Sp. gr. of liquor	1.21	
Percentage of NaOH in liquor	8.7	
Percentage of NaCl in liquor	15.3	
Caustic soda per cell per day	110	lb.
Chlorine per cell per day	98	lb.
Current per cell (approx.)	1,500	amp.
Voltage per cell	3.5	v.
Active anode surface per cell (approx.)	25	sq. ft.
Current density (approx.)	55	amp. per sq. ft.
Current efficiency	93	per cent
Power efficiency	62	per cent

The Vorce Cell—A comparatively recent development is the Vorce cell[33] which enjoys a very wide popularity in this country and which in certain cases is replacing the rectangular types of cells. The cell is shown in Figure 10 and the anode and cathode assemblies are shown separately in Figure 11. They are circular and compact and have much lighter weight per unit of output than the Allen-Moore cells. They are constructed of sheet steel in the cylindrical body 26 inches diameter, 42 inches high, and of concrete asbestos composition in the bottom and top. Inside the steel tank are the cathode iron screen and asbestos diaphragm, and inside the asbestos diaphragm is a circular row of 24 small graphite sticks (2 in. × 2 in. square) all suspended from the top, serving as an-

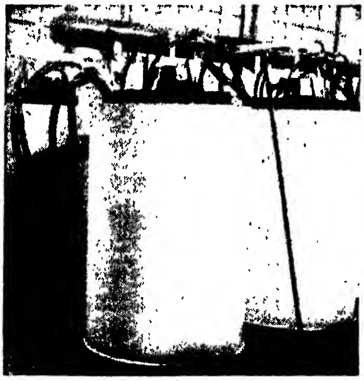

FIG. 10. The Vorce Cell. (Courtesy Dr. L. D. Vorce)

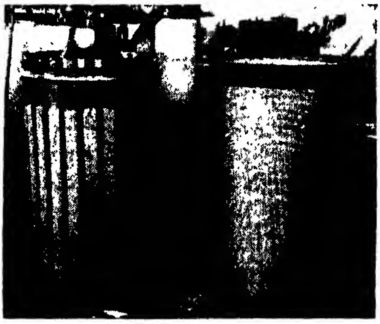

FIG. 11. Anode and Cathode Assemblies of the Vorce Cell. (Courtesy Dr. L. D. Vorce)

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[33] Vorce, L. D., "Unit Process and Principles of Chemical Engineering," edited by J. C. Olsen, p. 378, D. Van Nostrand Co., Inc., first edition (1932).

For further details about Vorce cells, see Hou, T. P., "Manufacture of Soda," Chapter XX, "Manufacture of Electrolytic Caustic, Chlorine and Chlorine Products," second edition, Reinhold Publishing Corp., New York (1942).

odes. The chief advantages of these cells are the saving in floor space; the greater active anode surface per unit cell volume; the integral construction of the anodes, eliminating joints; and the high purity in the chlorine gas obtained. The Vorce cells are now extensively used in the United States. The description of the operation of the Allen-Moore cells applies in a general way here and we shall not enter into any details in the method of operation, except mentioning that the life of the anodes is somewhat longer. Anode life may be increased by the treatment of the graphite with boiled linseed oil, although this causes a slight increase in the electrical resistance of the graphite. The repairs and renewals in these cells are greatly simplified and may be effected, if necessary, by lifting off the whole cell bodily.

A new development in the construction of the Vorce cells consists of introducing an extra cathode inside the row of graphite anodes, which adds more cathode surface and which also reduces the gap. This further reduces the terminal voltage per cell and eventually the average working voltage per cell may fall to below 3.0 volts, thereby increasing the power efficiency to above 70 per cent. The capacity of the cell then may be doubled by doubling the amperage without, however, exceeding the regular voltage of a standard cell.

The Hooker Type S Cell—Lately large units of diaphragm cells have been developed by Hooker Electrochemical Co. of Niagara Falls, N. Y., in the so-called S type[84] cell. It is a square type using concrete and steel construction as shown in Figures 12 and 13. Hence the name cubical cells. Their distinctive features are: the deposited asbestos diaphragm and closely packed alternate anodes and cathodes, so that the electrode surface is more nearly proportional to the cube, rather than the square, of the linear dimension. Further, the anode graphite blades are supported from the bottom, being embedded in a lead slab, and the cathode iron fingers, supported horizontally from the steel frame, project into the narrow spaces between adjacent anode blades. There are 30 of each of these electrodes arranged in two main rows, filling the space of the cell, with a central lane for the brine flow. The anodes are thus submerged in the brine, free from the top, so that the spacing between any adjacent electrodes inside the cell is closely set and may be checked before the cover is put on. The cell has a large output and high electrical efficiencies. The outside dimensions of the cell are 4 ft.-6 in. wide by 5 ft. long by 3 ft.-8 in. high. Typical operating results are given in Table 27.

TABLE 27—SOME TYPICAL OPERATING RESULTS OF HOOKER S CELL

Terminal voltage	3.28-3.45 v.
Current per cell	5,000-7,000 amp.
Current density, anode	55 amp./sq. ft.
Current density, cathode	47 amp./sq. ft.
Current efficiency	94-95 per cent
Energy efficiency	64-66 per cent
NaOH per KW-hr.	0.91-0.94 lb.
NaOH per cell per day	455 lb.
Chlorine per KW-hr.	0.84 lb.
Chlorine per cell per day	413 lb.
Life of anode	350-600 days
Life of diaphragm	175-250 days

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[84] Stuart, K. E., Lyster, T. D. B., and Murray, R. L., Chem. & Met., *45*, 354 (1938).

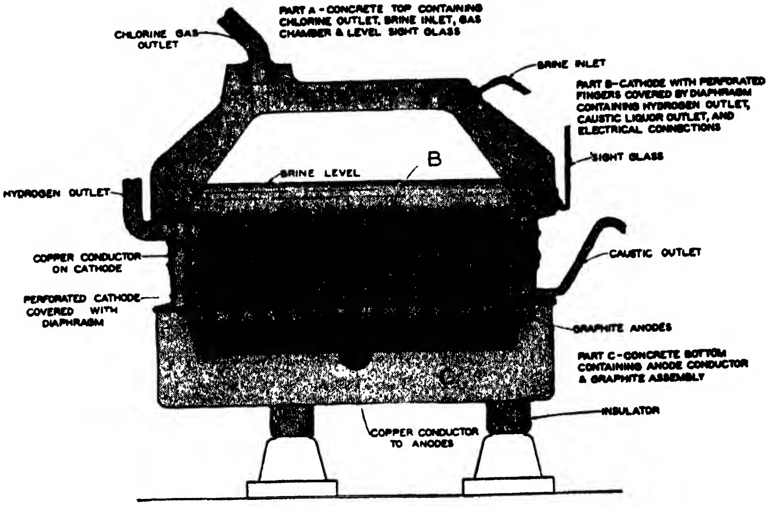

Fig. 12. Cross Section of Hooker Cell.

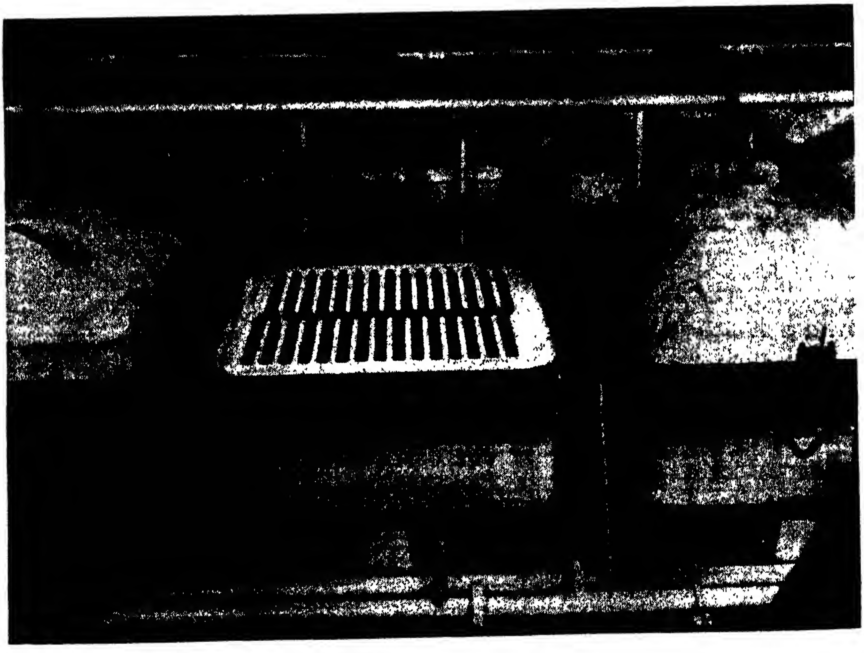

Fig. 13. Assembly of Hooker Cell.

The Mercury Cell—One of the earliest cells used for the electrolysis of brine was the Castner cell, wherein mercury acts as an intermediate electrode in place of a diaphragm. In the original Castner cell, the body is made of slate or concrete, the general dimensions being 4′ × 4′ × 6″ high. Graphite blocks are used as anodes placed at each end, while iron grids are used for cathodes in the central compartment. Mercury used as the intermediate electrode lies at the bottom. Brine is electrolyzed in each end compartment. Chlorine is liberated at the anode and the sodium metal liberated becomes amalgamated in the mercury. At intervals, the cell is rocked by a cam and the amalgam at each end compartment is allowed to come to the central compartment containing the iron cathode, where sodium metal reacts with water forming caustic soda solution, and hydrogen gas evolves. The terminal voltage of the cell is somewhat greater than for the cells previously described, being about 4.1 volts.

The particular advantage of this cell lies in the fact that it produces caustic solution free of sodium chloride, because the sodium hydroxide is formed by the reaction of the sodium amalgam with chloride-free water in the cathode compartment. The caustic concentration is also higher than for other cells, requiring less evaporation of water to produce marketable caustic. Despite these advantages, the original Castner cell had a checkered career. Its low energy efficiency and numerous mechanical difficulties rendered it practically obsolete for a time. But the demand in recent years for pure caustic, particularly by the rayon industry, gave impetus to its improvement. Modifications have been made and put into operation, particularly by the Mathieson Alkali Works, Inc. One of the modifications is the Sorensen type cell consisting of cast-iron frame lined with concrete. Another is the huge Krebs type cell using ebonite and iron frame, taking current up to 15,000 amperes per cell. In either of these newer types, mercury is used directly as the cathode, and the amalgam is sent to a denuding chamber for decomposition.

Cell Efficiencies. Considerable advance has been made in the construction and operation of the alkali-chlorine cells of the vertical diaphragm type, resulting in the reduction of cell voltage and in the increase of both power and current efficiencies. Power and salt are the two largest items of cost, accounting for two-thirds of the total cost of production in this electrolytic process, so it is imperative that power consumption (and consequently voltage per cell) be kept low and the utilization of salt (and consequently current efficiency) be continually improved. Figure 14 shows the trend of the reduction in the cell voltage for the last three decades. Figure 15 shows the improvement in the power and current efficiencies during the same period.

Evaporation of Caustic Solutions—The cell effluent is collected in liquor storage tanks from which it is pumped to evaporators for concentration. Zaremba, Swenson, or Buffalo Foundry evaporators of submerged vertical tube type[35] with salt catchers or separators are among the ones most generally used. Two effects (and sometimes three) are generally employed. According to the practice of one plant, each evaporator is 80 inches in diameter by 12 feet high, holding about 1000 gals. of the liquor. In the first effect, exhaust steam, or live

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[35] For more detail concerning the operation of this type of evaporator, see Chapters 2 and 9.

steam throttled to 25 lbs. pressure is employed, and the pressure above the liquor in the first effect varies from 3 to 5 lbs. gauge pressure. The liquor is sucked over to the second effect by vacuum where the vacuum above the liquor is about 27 in. Hg. Condensed steam from both effects goes back to the boiler as feed water. On top of the second effect (or last effect) is located a separator, to the outlet of which a barometric condenser is attached, with connection to a vacuum pump. In the second (or last) effect the caustic liquor is concentrated to as high as 47° Bé. (sp. gr. = 1.475), when most of the salt will have crystallized out. The analysis of a typical strong caustic from the evaporator is given in Table 28.

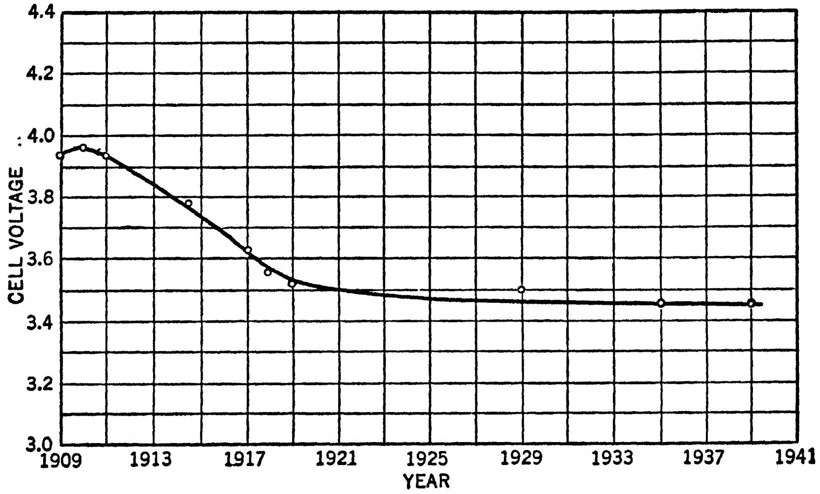

Fig. 14. Reduction in Cell Voltage.

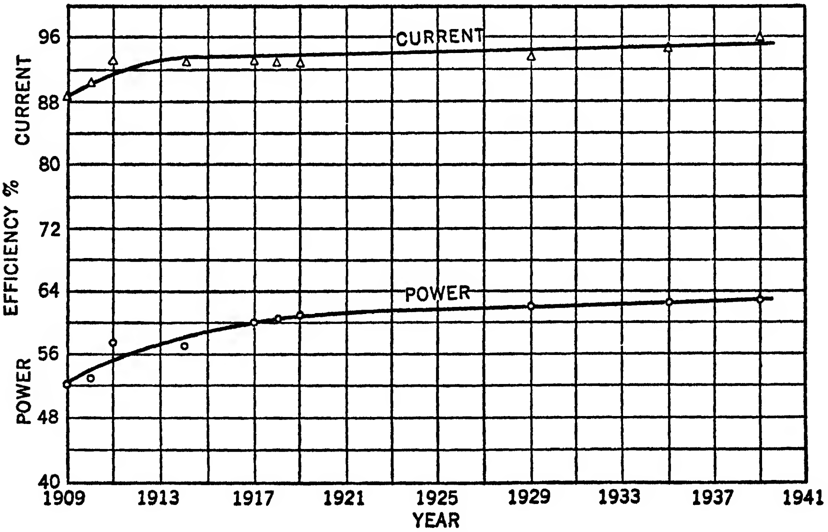

Fig. 15. Improvement in Cell Efficiencies.

TABLE 28—ANALYSIS OF STRONG CAUSTIC FROM EVAPORATOR

Sp. gr. at 25° C.	1.475	or 47° Bé.
NaOH	628	g. per l.
NaCl	47.2	g. per l.
Na_2SO_4	3.0	g. per l.

It will be seen that a great deal of the NaCl and Na_2SO_4 will have been separated from the strong caustic here. The strong liquor (47° Bé.) is drawn to water-jacketed settling tanks where, on cooling, more salt is separated out. If solid caustic is desired, this clarified 47° Bé. caustic is decanted and further concentrated in cast-iron open pots by direct fire for two to three days. The molten caustic is then ladled to steel drums, as explained under caustic soda manufacture.[36]

The salt from the catchers is washed until it contains about 0.1 per cent NaOH, when it is dissolved with warm water and the solution used for treating raw brine in conjunction with soda ash treatment. The wash water is sent back to the evaporators with the weak liquor. When these NaCl and Na_2SO_4 crystals are dissolved up and sent back to the raw brine treating tanks, the Na_2SO_4 will accumulate in the brine, causing low efficiency in the cells. To get rid of Na_2SO_4, when necessary, $BaCl_2$ solution may be employed.

As the evaporator tubes are often made of steel, any hypochlorite carried in the weak liquor (or cell effluent) will attack these tubes very rapidly, causing corrosion in the steam chest and leaks in the tubes. It cannot be too strongly emphasized that all efforts must be made to keep the cell effluent free from hypochlorites, or the upkeep on the evaporators will be heavy. If proper attention is given to the operation of the cells, these tubes should last for more than two years.

Nickel tube evaporators are far more satisfactory and are being increasingly used. They are especially recommended where high pressure steam is employed and high concentration of caustic liquor is to be obtained. With 75 lb. pressure steam it is possible to concentrate liquid caustic in nickel tube evaporators to 60-70 per cent NaOH.

Manufacture of Liquid Caustic—Caustic liquor of about 50 per cent NaOH obtained from the last effect of the evaporators or from the final evaporator is also sold directly as liquid caustic to the rayon industries. Because of the very stringent requirements regarding the purity of the caustic, an attempt is sometimes made to produce liquid caustic which is practically free from salt. The 50 per cent caustic after complete settling and decantation is again diluted to about 37° Bé. and cooled to about 3° C. when hydrated caustic crystals of $NaOH \cdot 3\frac{1}{2}H_2O$ and $NaOH \cdot 4H_2O$ separate out, leaving salt in solution. These hydrated crystals of caustic are then filtered off and melted by heating, and the solution is again brought to 50 per cent concentration by evaporation and sold as pure liquid caustic. This operation for removal of salt is not necessary for caustic made in the mercury cells. This recrystallization operation also removes some of the impurities, such as iron salts which may come from corrosion of steel evaporator tubes and bodies. Liquid caustic for rayon manufacture is now made by several manufacturers in all-nickel evaporators in which not only tubes are

[36] See p. 432.

made of nickel but also evaporator sections themselves. Other equipment handling the caustic liquors, such as coolers, storage tanks, etc., may be nickel-clad, while pumps may be made of stainless steel. This eliminates the possibility of getting iron in the solution and makes a better rayon quality caustic.

The production of solid caustic was described on page 432.

Preparation of Liquid Chlorine—The list of the uses of the chlorine produced by the electrolytic cells is growing with extreme rapidity. The manufacture of hydrochloric acid from chlorine has been described previously.[37] Its utilization in the bleach industry and in organic and inorganic syntheses is handled in subsequent chapters.[38]

One of the interesting industrial developments of recent years has been the great expansion in the use of liquid chlorine for many purposes. To produce liquid chlorine the gas is kept as rich as possible by avoiding air leakages and excessive vacuum in the main. The gas is first dried by passing up through a tile-packed stoneware tower, with 93 per cent sulfuric acid passing down countercurrently. The gas is pulled through the drying tower by means of a rotary pump, such as Nash "Hytor," using also 93 per cent acid as seal. Each pump can develop a pressure as much as 25 lbs. gauge, compressing the chlorine gas through a refrigerating system kept at a temperature of about −12° C. Chlorine gas under this pressure and at this temperature is liquefied. The dry liquid chlorine may be safely handled in steel cylinders containing 100-150 lbs. each, or in steel tank cars.

READING LIST

THE AMMONIA-SODA INDUSTRY

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[37] See Chapter 9.

[38] See Chapters 11 and 28.

CHAPTER 11

CHLORINE PRODUCTS

R. B. MacMullin, Assistant Director of Research
and
C. A. Hampel, Mathieson Alkali Works, Inc.

The list of products made by chemical methods in which chlorine is one of the reactants contains a very large number of items. But the group is so important, both as raw materials for other chemical industries and for consumer use, that it is worth while to devote a chapter to their production. This will be confined to brief descriptions of the processes used and short discussions of the uses. The variety of the uses demonstrates clearly the interdependence of the many branches of chemical industry.

Chlorine products may be divided into 3 classes.

(1) Hypochlorites, chlorites, chlorates and perchlorates.
(2) Inorganic chlorides.
(3) Organic chlorination products.

HYPOCHLORITES, CHLORITES, CHLORATES AND PERCHLORATES

Hypochlorites—The salts of hypochlorous acid (HOCl) are important oxidizing agents, being used extensively in bleaching textiles, in laundering, water sterilization, preservation of food, and sanitation. Statistics on total production of hypochlorite in all forms are not available, but it is certain that a large part of all the chlorine made is used in the form of hypochlorite.

The formation of hypochlorites from chlorine is illustrated by the following reactions:

$$Cl_2 + H_2O = HOCl + HCl$$
$$Cl_2 + 2NaOH = NaOCl + NaCl + H_2O$$
$$2Cl_2 + 2Ca(OH)_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O$$

In all cases the (OCl) radical is equivalent to a molecule of elemental chlorine (Cl_2) in oxidizing power, and the chlorine may always be regenerated from the hypochlorite by acidification (reversal of the first equation). It has become accepted practice to speak of the strength of hypochlorite preparations in terms of "available chlorine," by which is meant the Cl_2 equivalent of the (OCl) present. Hypochlorite chlorine is electropositive in character, and has a valence of plus one, in distinction to chloride chlorine, which is electronegative and has a valence of minus one, so it is a bivalent oxidizing agent. Hence, pure calcium hypochlorite ($Ca(OCl)_2$) having a molecular weight of 142.99, contains the equivalent of $2Cl_2$ molecules weighing 141.84, and would therefore contain

141.84/142.99 = 99.19 per cent "available chlorine." The oxidation reactions of chlorine and of hypochlorite may be written:

$$Cl_2 + 2e \rightarrow 2Cl^-$$
$$Cl^{+1} + 2e \rightarrow Cl^{-1}$$

Bleaching Powder—In 1799 Charles Tennant took out a patent in England for producing a bleaching compound by the absorption of chlorine gas by hydrated lime. The product contained about 30-40 per cent available chlorine and approximated the formula $CaCl(OCl) \cdot CaO \cdot 2H_2O$. In the early days, the chlorine was obtained in dilute form from either the Weldon or the Deacon process, and the lime served to fix the chlorine into a convenient solid form. Shortly after the introduction of the electrolytic chlorine process (1892) chlorine was liquefied (1909 in the United States) and from that time on more and more of the chlorine produced came to be used in liquefied form, and less and less as bleaching powder. Because of the unstable character and low test of bleaching powder, true calcium hypochlorite was developed and put on the market in 1928, so that today, the manufacture of bleaching powder is markedly decreasing.

Bleaching powder is made by either the chamber process or a continuous mechanical process. In the chamber process the moist chlorine gas, generally diluted with air, is passed through a series of lead chambers until the chlorine is all absorbed. The lead chambers are typically 20 feet wide, 100 feet long, and 7 feet high, and usually have concrete floors in which are imbedded cooling coils through which is circulated refrigerated brine. Hydrated lime is spread by hand on the floor of the chambers to a depth of about 3 inches, and this is then furrowed. Several chambers (typically ten) are connected in series. When the bleach in number one chamber has reached 35 to 40 per cent available chlorine, it is cut out of the series, and blown out with air until the atmosphere is sweet. The chamber is then opened, and men wearing gas masks or dust masks then push and shovel the finished bleach through discharge ports in the floor into barrels or drums. After spreading a new layer of lime, the chamber is closed, and made the end chamber of the series. To make a ton of bleaching powder per day, a chamber area of about 1400 square feet is required. The limiting factor in rate of production is usually the temperature, which must be kept below 45°C.

Mechanical bleach machines were developed to eliminate the unpleasant labor connected with the chambers, and to save space and expensive lead. These machines are horizontal rotary steel tubes, tile lined and water cooled on the outside. Machines built along the lines of the Herreschof furnace have also been used.

Bleaching powder is unstable to heat, and the moisture and CO_2 of the atmosphere will decompose it. Even when stored under favorable conditions, bleaching powder tends to lose most of its available chlorine in a year's time. Its stability can be somewhat improved by mixing it with quicklime, CaO, which has the effect of removing the free moisture. In this form, containing around 25 per cent available chlorine, it is known as "tropical bleach." Bleaching powder is still made for industrial use because of its low cost of manufacture, and because in such application it is used promptly.

Calcium Hypochlorite—The development of true calcium hypochlorite, containing at least 70 per cent available chlorine, and having very good stability, has still further displaced the older bleaching powder. First produced by Griesheim Elektron Fabrik about 1923 in Germany under the name of "Perchloron" and shortly after in the United States by Mathieson Alkali Works, Inc., under the trade name "H.T.H." (High Test Hypochlorite), it is now being produced in several countries and by several different processes.

German Process.[1] A thick lime slurry is chlorinated under pressure, most of the chlorination being done at 30-40° C. to avoid formation of undesired basic salts.

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + H_2O$$

The $CaCl_2$ remains soluble, while a good part of the $Ca(OCl)_2$ is forced out of solution as the crystalline dihydrate. The slurry is difficultly filterable, so that it is given a final filtration in a hydraulic press in order to squeeze out as much $CaCl_2$ as possible. The product is then dried to about 1-4 per cent H_2O content. The product, known as "Perchloron," has, as its chief impurities, lime and other insoluble matter introduced with the lime, and also a little $CaCl_2$.

Mathieson Process.[2] Equivalent amounts of lime and caustic soda are chlorinated (in solution), according to the reaction:

$$Ca(OH)_2 + 2NaOH + 2Cl_2 = Ca(OCl)_2 + 2NaCl + 2H_2O$$

Above 16° C. the difficultly filterable $Ca(OCl)_2 \cdot 2H_2O$ would crystallize, but below this temperature, the stable phase is the triple salt $Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O$. After chlorination is complete, the slurry is cooled with mechanical refrigeration to about $-10°$ C. to obtain a high yield of the triple salt. This compound grows in the form of solid hexagonal prisms and it is easily separated from the mother liquor and the insoluble slimes by centrifuging. The triple salt itself is unstable at ordinary temperature, and cannot be dried without considerable decomposition. It is therefore converted to the more stable calcium hypochlorite by reacting it with a specially prepared chlorinated lime slurry, in such proportion that the $CaCl_2$ of this slurry is equivalent to the NaOCl content of the triple salt, thus:

$$2Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O + CaCl_2 + Ca(OCl)_2 = 4Ca(OCl)_2 \cdot 2H_2O + 4NaCl + 16H_2O$$

The slurry is then dewatered to remove salt, and the product is dried. The coarse granular type of product is made by drying in vacuo, while the powdery form is obtained by spray drying in hot air.

Columbia Process.[3] Very recently another American process has reached the commercial stage. In this process, chlorine gas, diluted with air and CO_2, is passed over solid sodium bicarbonate or carbonate. Chlorine monoxide gas is liberated according to the reaction:

$$2Cl_2 + 2NaHCO_3 \rightarrow Cl_2O + 2NaCl + 2CO_2 + H_2O$$

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[1] Pistor and Reitz, U. S. Patent 1,236,978 (Aug. 14, 1917) to Griesheim Elektron Fabrik. Operated now in the United States by The Pennsylvania Salt Mfg. Co., Philadelphia, Pa.

[2] U. S. Patents Nos. 1,754,474; 1,787,048; 1,713,650; 2,195,755. Developed by the Mathieson Alkali Works, Inc., New York, N. Y.

[3] U. S. Patent No. 2,157,524. Developed by Columbia Alkali Division of Pittsburgh Plate Glass Co., Barberton, Ohio.

The dilute gas is passed through ice water, which dissolves the Cl_2O to produce a 10-15 per cent solution of hypochlorous acid, in which the other gases are difficultly soluble: $Cl_2O + H_2O \rightarrow 2HOCl$. This acid is neutralized with lime (at a low temperature to prevent decomposition) and the resulting solution of calcium hypochlorite is filtered, and then spray dried.

Japanese Process.[4] Milk of lime is partly chlorinated, and dibasic calcium hypochlorite ($Ca(OCl)_2 \cdot 2Ca(OH)_2$) separates as hexagonal plates, which are settled and centrifuged free of the chloride-containing mother liquor. The dibasic crystals are then decomposed with water, and the lime is filtered off to be chlorinated in a repetition of the cycle. The weak calcium hypochlorite solution is concentrated by evaporation in vacuo and dried. In a variation of this process, bleaching powder is stirred into strong bleach liquor, forming a precipitate of $Ca(OCl)_2 \cdot 2H_2O$ and basic salts, which are filtered off and dried.

Imperial Chemical Industries Process (English).[5] Dibasic calcium hypochlorite is first prepared in hexagonal plates. Part of this is obtained by partial chlorination of lime, and the balance by mixing milk of lime slurry with filtrates of high available chlorine content. The basic salt is separated by centrifuging, suspended in water and chlorinated until most of the lime is used up:

$$Ca(OCl)_2 \cdot 2Ca(OH)_2 + 2Cl_2 = 2Ca(OCl)_2 + CaCl_2$$

Most of the calcium hypochlorite is precipitated as the dihydrate. Because this forms from a solution of low calcium chloride concentration, the crystals are larger than those obtained in the German process and hence are easier to filter. The crystals are filtered off and dried. The filtrate is then treated with milk of lime to form more of the dibasic salt and a liquor low in available chlorine content, which must be used for other purposes or discarded.

Thann Process (French).[6] Dibasic calcium hypochlorite is added to a calcium hypochlorite-calcium chloride brine, in which it is chlorinated. Further additions of the dibasic salt and of water are made at intervals, and portions of the slurry are withdrawn for filtration when the calcium hydroxide is nearly all used up. Proportions are chosen to keep the slurry quite thin, much of the filtrate being returned to the chlorinator for this purpose. The surplus filtrate is treated with an excess of lime, and the resulting slurry is partly chlorinated to produce the dibasic salt required in the process, and a byproduct liquor of low available chlorine content. The crystals of calcium hypochlorite dihydrate are fairly well formed, due to the dilution of the slurry they are grown in. The available chlorine in the waste liquor is less than that in the Imperial Chemical Industries process.

Bleach Liquor—A very large part of the chlorine used in bleaching pulp is actually used in the form of a calcium hypochlorite solution. In the usual procedure, milk of lime is put into a concrete tank, and then circulated through an outside centrifugal pump. Liquid chlorine is introduced into the suction side of the pump at such a rate that the lime is not overchlorinated. Sweep agitators are used to keep the lime in suspension, and lead cooling coils are used to mini-

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[4] Urano, Saburo, Trans. Am. Electrochem. Soc., *49*, 65-73 (1926) and Jap. Patent 92,909.

[5] British Patents Nos. 378,847 and 404,627.

[6] British Patent No. 487,009.

mize decomposition from overheating. When finished, the tank is settled, the clear bleach liquor is pumped off, and the sludge is washed with water before discarding. The usual concentration of calcium hypochlorite bleach made in this way is 30 to 80 grams per liter of available chlorine. Basic compounds are first formed if the available chlorine content is 100 grams per liter or higher. A liquor containing more than about 170 grams per liter would settle with difficulty. The finished liquor should be slightly alkaline to phenolphthalein (flash test), and not over 25-30° C. in temperature. Low magnesia lime, well burnt and quick-settling, is preferred for this use. Bleach liquor decomposes at a rate of 1 to 2 grams per liter per week in the winter and faster in the summer time.

Sodium Hypochlorite—Relatively stable solutions can be made, but solid sodium hypochlorite, either hydrated or dry, is unstable and not commercially available. Solutions are made by chlorinating caustic soda, or sometimes soda ash, in ceramic, glass lined, or rubber lined tanks. For commercial use the usual strength made is 10 to 15 per cent available chlorine. Household bleach solutions usually contain 3-5 per cent available chlorine. The temperature should be kept at about 35° during chlorination, and a slight excess of alkali must be left in the solution to stabilize it. Over-chlorination will cause rapid decomposition to chlorate and chloride by the reaction $3NaClO = NaClO_3 + 2NaCl$. Iron, copper, manganese, in fact most metals, will render the solution unstable, even if only traces are present.

Preparation from Calcium Hypochlorite. Sodium hypochlorite solutions are readily prepared from calcium hypochlorite by the addition of soda ash or sodium sulfate:

$$Ca(OCl)_2 + Na_2CO_3 = CaCO_3 + 2NaOCl$$

After the carbonate has settled, the sodium hypochlorite is decanted off. Ready mixed preparations of this sort, in dry form, are available on the market. The original "Javelle water" of antiquity was made from bleaching powder solutions by the addition of potassium carbonate, in a similar manner.

Electrolytic bleach is the name generally applied to solutions of sodium hypochlorite prepared by electrolysis of salt solutions. Only weak solutions can be efficiently prepared, containing 15 to 35 grams per liter of available chlorine. Installations of this kind are therefore located at the point of use, generally in the bleaching departments of textile mills.[7] Electrolytic bleach was popular before the advent of liquid chlorine, but today there are no installations in the United States and not many in Europe.

Alkyl Hypochlorites—Hypochlorous acid reacts with most alcohols to form alkyl hypochlorites, which are, for the most part, oils insoluble in water. Only the tertiary alkyl hypochlorites are sufficiently stable to be commercially interesting. Tertiary butyl hypochlorite is prepared by over-chlorinating sodium hypochlorite solution in the presence of the alcohol:

$$NaOCl + Cl_2 + 2C_4H_9OH = NaCl + 2C_4H_9OCl + H_2O$$

The oil is readily separated from the salt solution.

Uses for Hypochlorite—Bleach liquor (calcium hypochlorite solution) is made and consumed in large quantities by the paper mills for bleaching the

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[7] See Chapter 29.

pulp.[8] In the textile industry the vegetable fibers, chiefly cotton and rayon, are bleached [9] both in the form of yarn and finished goods, with a "chemic" containing hypochlorite. Sodium hypochlorite is extensively used in laundries [10] for whitening the goods right in the wash wheel.

Because of its germicidal properties, hypochlorite is used for water purification, especially in remote locations where liquid chlorine is unobtainable, or in cases of disaster when the safe municipal water supply is cut off. It is of importance in surgery, where the 0.5 per cent NaOCl solution with carefully adjusted pH, known as Dakin's solution, is used to sterilize open wounds and incisions. Hypochlorite is used for many other sanitary purposes, including treatment of night soil, dusting poultry, killing fungus, disinfecting swimming pools, sterilizing cold storage rooms, and sterilizing dairy equipment.

Hypochlorites also find many chemical uses as an oxidizing agent, notably in petroleum refining, manufacture of dyestuffs,[11] and preparation of oxygen gas. The alkyl hypochlorites have found limited use in shrink-proofing wool, manufacture of pure calcium hypochlorite, and in organic synthesis.[12]

Certain inorganic compounds, such as tri-sodium phosphate, have the ability to hold a small percentage of sodium hypochlorite in solid solution, and these substances are relatively stable. They are used as cleansers and detergents.

CHLORITES

The salts of chlorous acid ($HClO_2$), known as chlorites, have not been commercially available until quite recently (1940). Sodium chlorite is a powerful oxidizing agent, and contains, when pure, 156.9 per cent "available chlorine." The commercial product contains about 80 per cent $NaClO_2$ or 125 per cent available chlorine. Chlorites will bleach cellulosic materials both on the alkaline and on the acid side. They have a strong affinity for sulfur, sulfides and sulfites, and will attack rubber vulcanized with sulfur. Sodium chlorite is readily soluble in water, a saturated solution containing 39 per cent $NaClO_2$ at 17° C. The solid is not deliquescent and is completely stable when stored under ordinary conditions. Solutions are quite stable if kept neutral or slightly alkaline, although they decompose very slowly on boiling. Chlorites are decomposed by acids, with liberation of chlorine dioxide gas:

$$5NaClO_2 + 2H_2SO_4 = 4ClO_2 + NaCl + 2Na_2SO_4 + 2H_2O$$

and by chlorine, also with liberation of chlorine dioxide gas:

$$2NaClO_2 + Cl_2 = 2NaCl + 2ClO_2$$

Manufacture—A process has been developed by the Mathieson Alkali Works [13] which utilizes lime, chlorine, caustic soda and carbon. Lime and

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[8] See Chapter 37.
[9] See Chapter 29.
[10] See Chapter 42.
[11] See Chapter 28.
[12] See Chapter 3.
[13] U. S. Patents Nos. 2,092,945; 2,036,375; 2,036,311; 2,031,681; 2,092,944; and 2,108,976. All to Mathieson Alkali Works, Inc.

chlorine are first converted to calcium chlorate by over-chlorination at elevated temperatures:

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O \qquad (1)$$

The chlorate liquor is then treated with hydrochloric acid in the cold:

$$Ca(ClO_3)_2 + 4HCl = CaCl_2 + 2ClO_2 + Cl_2 + 2H_2O \qquad (2)$$

The liberated gases, diluted with air, are contacted with lime, which preferentially absorbs the chlorine. This lime is then used in reaction (1). The chlorine dioxide is then removed from the air stream by scrubbing with a caustic soda solution in the presence of carbonaceous matter and lime:

$$4NaOH + Ca(OH)_2 + C + 4ClO_2 = 4NaClO_2 + CaCO_3 \downarrow + 3H_2O \qquad (3)$$

After filtering, to remove the $CaCO_3$, the solution of $NaClO_2$ is evaporated and drum dried.

Uses—Sodium chlorite is now being used commercially in bleaching paper pulp. Kraft pulp can be bleached to a high whiteness without loss of strength. In practice, the pulp purification process[14] is carried as far as possible without damage to the fiber using chlorine and hypochlorite; then the chlorite bleaching process is applied to finish the pulp to a high white, while preserving strength.

Chlorite is also used in the bleaching and finishing of cotton, rayon and celanese. It is commonly used in acid conditions along with a detergent to obtain a scouring and bleaching in one step. It is also employed under extreme alkaline conditions at high temperature in the kiering operation where it is effective in starch and mote removal. It is of value in the bleaching of linen, wood surfaces, straw, oat hulls, ramie and hemp, and in the purification of cotton linters. It is a convenient source of pure chlorine dioxide (see previous equations) which is useful in pulp purification, flour bleaching and fungicide for fruit. Chemically pure $NaClO_2$ is also used as an analytical reagent in the determination of sulfur compounds.

CHLORATES

The salts of chloric acid ($HClO_3$) are called chlorates. They are powerful oxidizing agents under certain conditions, but do not liberate "available chlorine" as do the hypochlorites and chlorites, and hence cannot be used for bleaching. Potassium chlorate is an essential ingredient in making matches, and sodium chlorate is now extensively used in controlling weeds in agriculture.

Chlorates have been made at Niagara Falls since 1897.[15] Recently announced is a new chlorate plant[16] in the state of Oregon, which will utilize Bonneville hydroelectric power. The United States consumption of sodium, potassium, and barium chlorates taken together amounted to about 16,000 tons in 1935, and has been increasing steadily since. About 25 per cent of this consumption was formerly imported, chiefly from Germany and France. Present producing capacity is now sufficient for domestic needs. Abroad the chief chlorate-producing countries are Sweden, Germany, France, Italy and Japan.

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[14] See Chapter 37.

[15] Oldbury Electrochemical Co., Niagara Falls, N. Y.

[16] Pennsylvania Salt Co., Tacoma, Washington.

Manufacture—Chlorates are made directly or indirectly by the electrolysis of chlorides. Direct electrolysis is generally known as the "electrolytic method," while those processes which use chlorine and alkali are generally known as "chemical methods." Either sodium or potassium chlorate may be made in the same electrolytic cells, but the method of recovery of the chlorate crystals will differ, because of the different solubilities of the sodium and potassium systems. In the chemical process, calcium chlorate is first made, which can be converted to potassium chlorate, but not sodium chlorate. Barium chlorate can be prepared from either sodium or potassium chlorate by double decomposition. The processes now to be described are typical, although many variations would be found between different plants.

Electrolytic Methods—The fundamental reaction is

$$NaCl + 3H_2O + 6 \text{ Faradays} = NaClO_3 + 3H_2$$

Actually caustic soda is liberated at the cathode, and chlorine at the anode. However, since there is no diaphragm in the chlorate cell, mixing occurs, and these primary products react to form chlorate and some hypochlorite. For the most efficient production of chlorate the pH of the electrolyte is controlled in order to insure the presence of hypochlorous acid, which then reacts with the sodium hypochlorite to produce chlorate. The concentration of HCl in the electrolyte is generally kept at about 5 grams per liter. To protect steel parts of the cell, and other steel apparatus in contact with the electrolyte, it is now common practice to maintain a concentration of about 2 grams per liter of sodium dichromate in the liquor, which inhibits corrosion.

Cell bodies are generally made of steel, which in some types, are cement lined. They may also be of stoneware, or may be lead lined. The cathodes are nearly always of steel. The tank walls may also form part of the cathode surface. Cathodes may be in the form of steel plates, steel wire screen, or steel pipes, through which cooling water is circulated. Anodes may be in the form of graphite plates or rods, platinum or platinum-iridium wire, or fused-magnetite-covered copper rods. The cathode and anode surfaces are usually arranged in close proximity, cathodes alternating with anodes in parallel vertical planes. Chlorate cells are generally water cooled.

Operating Characteristics. Operating conditions vary in different installations. In certain European plants only 30-50 per cent of the salt is converted in one passage through a bank of cells. In other plants 65-75 per cent of the salt is converted. The cells may be operated batchwise or continuously. The theoretical cell voltage is 1.6 volts, but in practice 2.8 to 3.5 volts are required. The best current density on the anode, according to Groggins,[17] is from .2 to .3 amperes per square inch; on the cathode, about .1 ampere per square inch. The lower the temperature the more favorable the current efficiency. At 44° C., the current efficiency is 75-80 per cent; at 25° C., 80-85 per cent. The power required is about 3 to 3.3 kilowatt hours per pound of either $KClO_3$ or $NaClO_3$.

Recovery of Chlorate. The liquor fed to the cells contains about 125 grams per liter $NaClO_3$ and 235 grams per liter of NaCl. The liquor from the cells

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[17] Groggins, P. H., and Associates, Chem. & Met. Eng., *44*, 302 (1937), and *45*, 692 (1938).

will contain, typically, 500 grams per liter of $NaClO_3$ and 70-80 grams per liter of NaCl. There are three possible ways to recover the chlorate:

1. By evaporation hot, throwing out NaCl until the solution is saturated with $NaClO_3$, followed by cooling to room temperature to crystallize the $NaClO_3$. This method is not suitable for $KClO_3$.
2. By chilling the cell liquor to crystallize the $NaClO_3$ or $KClO_3$.
3. By salting out the chlorate by addition of NaCl or KCl.

A typical plant, operating by the third method, dissolves rock salt in the cell liquor at 44° C. This liquor is then filtered to remove carbon particles and slime. The filtered liquor is cooled to 20° C., and $NaClO_3$ crystallizes. The crystals are centrifuged, dissolved in hot water and recrystallized, the second mother liquor being recycled. The pure crystals are washed, dried and ground. The first mother liquor is then recycled through the cells.

Consumptions in a plant making 250 tons $NaClO_3$ per month would be, per ton of $NaClO_3$, about as follows: salt, 0.60 ton; graphite, 20 pounds; hydrochloric acid, 35 pounds; sodium dichromate 10 pounds; electric power 6600 kilowatt hours; labor, 20 to 30 man hours.

Chemical Method—Calcium chlorate is first made by countercurrent chlorination of milk of lime in towers or closed agitated tanks. In all except the last tank, the chlorine is absorbed to form calcium hypochlorite. The temperature should be above about 40° C. to prevent the formation of insoluble basic compounds, but not above about 55° C., where decomposition with loss of oxygen begins to be serious. In the last tower the solution is over-chlorinated, and under these conditions, at about 70° C., the hypochlorite is efficiently converted to calcium chlorate. The solution is then filtered, and should contain at least 125 grams per liter of $Ca(ClO_3)_2$, and not over 5-10 grams per liter of $Ca(OCl)_2$. The reaction system may be made of cast iron, lead, rubber-lined steel, or stoneware. The chemical efficiency is 95 per cent.

Pulverized potassium chloride is now added to the calcium chlorate liquor. KCl dissolves and $KClO_3$ crystallizes out on chilling with artificial refrigeration. The crude $KClO_3$ is centrifuged, redissolved, and recrystallized, and the mother liquor from the last step is recycled. The pure $KClO_3$ is carefully dried and ground (for match manufacture). Aluminum apparatus is extensively used on the potassium end of the process.

Consumptions, per ton of $KClO_3$, will run about as follows: KCl (98 per cent), 0.7 ton; lime (96 per cent CaO), 2.0 tons; chlorine 2.16 tons; coal, for heating, crystallizing, drying, 0.035 ton; labor, 4 to 6 man hours.

Uses for Chlorates—Sodium chlorate is now used extensively as a weed killer. It is probably the most efficient general herbicide available, being useful in practically all climates and soils. It is not used for explosives because of its deliquescent properties. It is used in textile dyeing and printing and for bleaching certain inorganic acids.

Potassium chlorate, when mixed with dry organic matter, is a dangerous explosive. It is used extensively in the manufacture of matches, fireworks, explosives, ammunitions. It is used in the manufacture of paper, dry colors, inks and dyestuffs. It is also used as a general antiseptic in medicine.

Barium chlorate is used in the manufacture of fireworks. Ammonium chlorate is not stable. Calcium chlorate is used in the manufacture of potassium chlorate, and in the manufacture of sodium chlorite. It is also used to some extent as a weed killer.

PERCHLORATES

The salts of perchloric acid ($HClO_4$) are the most stable of all the oxychloride salts in the series hypochlorite-chlorite-chlorate-perchlorate. The salt usually first manufactured is sodium perchlorate, but because of its extreme solubility in water, it is usually converted to the perchlorate of other metals, such as potassium, barium, strontium or ammonium, for commercial application.

Sodium perchlorate is made by the electrolysis of sodium chlorate, according to the reaction $NaClO_3 + H_2O + 2 \text{ Faradays} = NaClO_4 + H_2$. The cells used are quite similar to the chlorate cells described in the previous section. Perchlorate cannot be efficiently made directly from salt. Starting with sodium chlorate, a high current density, preferably 4-8 amperes per square inch on the platinum anodes, is used. The electrolysis is usually carried out batchwise, and the current efficiency is high at the start, falling off at the end, but with an average value of about 85-95 per cent. Water cooling the cells improves the current efficiency but increases the voltage (5.25 to 6.45 volts). Starting with a chlorate concentration of about 645 grams per liter, the electrolysis will bring the chlorate down to about 5-50 grams per liter, with an overall energy consumption of about 1.3 to 1.6 kilowatt hours per pound of sodium perchlorate.

Potassium perchlorate is the least soluble of the perchlorate salts and is readily prepared by the addition of KCl to a solution of $NaClO_4$. This salt is stable in air. Ammonium perchlorate is prepared by double exchange with NH_4Cl or $(NH_4)_2SO_4$. Its solubility changes markedly with temperature, so that it is easily crystallized from water. Because of the volatile nature of the products of combustion of ammonium perchlorate, it is one of the most valuable of the perchlorate salts for use in explosives. Other perchlorates, such as barium and strontium, are used extensively in the manufacture of fireworks and flares.

Perchloric acid is prepared by distillation of $KClO_4$ with concentrated H_2SO_4 in a vacuum; or by reaction with hydrofluosilicic acid:

$$2KClO_4 + H_2SiF_6 = K_2SiF_6 + 2HClO_4$$

The K_2SiF_6, which is only slightly soluble, is filtered off, and the perchloric acid is purified by distillation. In this country, commercial strength runs 70-72 per cent $HClO_4$. Perchloric acid is chiefly used as an analytical reagent.

INORGANIC CHLORINATION PRODUCTS

Chlorine is used to prepare the chlorides of many elements, and, in some cases, to effect separations in metallurgy. The principal methods are four in number:

1. Direct addition of chlorine to the element.
2. Chlorination by means of an intermediate chlorine compound, such as S_2Cl_2, $COCl_2$ or HCl.
3. Chlorination of the oxide in presence of carbon.
4. Substitution of chlorine for another element (usually sulfur) in a compound.

The conditions of chlorination vary widely. Most metals react with dry chlorine gas energetically at elevated temperatures, a few in the cold; most metals are attacked by chlorine in the presence of moisture, even in the cold. Some elements are more readily chlorinated in the presence of sulfur. By way of illustration a number of the industrially important inorganic chlorinations will be described.

Aluminum Chloride—The usual procedure in making this compound, $AlCl_3$, is to blow chlorine gas into a bath of molten aluminum metal in a refractory crucible. The reaction is strongly exothermic, the heat liberated being sufficient not only to melt additional solid scrap or pig aluminum but to volatilize the $AlCl_3$ as fast as it is made. ($AlCl_3$ sublimes at 178° C.) The process is thus continuous. The $AlCl_3$ condenses out as a sublimate in an air cooled iron condenser, from which it is removed from time to time. The product is usually straw colored because of the presence of traces of $FeCl_3$.

Aluminum chloride may also be prepared by the chlorination of bauxite in the presence of carbon, according to the equation

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO$$

This reaction is endothermic, at temperatures necessary for reaction, and a temperature of 600-700° C. must be maintained by supplying heat. A better way is to use carbon monoxide instead of carbon; the reaction then becomes slightly exothermic and thus easier to control. The addition of a small amount of metallic aluminum to the bauxite will also serve to maintain reaction temperature.

Aluminum chloride solutions are readily prepared by action of hydrochloric acid on the metal or the oxide.

Uses. Anhydrous aluminum chloride is the condensing agent used in the Friedel-Craft reaction, which has extensive application in organic chemical synthesis and in petroleum refining. In the latter case, heating or "cracking" in the presence of $AlCl_3$ causes unsaturated compounds to condense to form saturated compounds, while high boiling compounds are converted to lower boiling compounds.[18] $AlCl_3$ also causes the liberation of H_2S from hydrocarbons containing sulfur. In recent years the Houdry process[18] of vapor phase cracking has to a great extent superseded liquid phase cracking, so that the use of $AlCl_3$ for this purpose has fallen off considerably.

Aluminum chloride is used as a catalyst in the Wahl-Gibbs-Conover Process for phthalic anhydride, and in the Friedel-Craft synthesis of anthraquinone. Solutions of $AlCl_3$ are used as astringents, and in prevention of putrefaction. Anhydrous $AlCl_3$ is a catalyst in organic chlorinations, playing the role of chlorine carrier.

Antimony Trichloride—$SbCl_3$, m.p. 73° C., b.p. 223° C. Pieces of antimony metal are added to a molten bath of the trichloride, and chlorine is blown into the bath. As the volume of $SbCl_3$ increases it is withdrawn from time to time. The reaction is strongly exothermic, and the problem is to keep the bath above the melting point of the chloride, yet below the melting point of the metal. A variation of the above procedure which permits close temperature control is to carry out the chlorination in a solvent such as carbon tetrachloride, in which

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[18] See Chapter 14.

the $SbCl_3$ dissolves. It then becomes a simple matter to recover the $SbCl_3$ by fractional distillation. Antimony trichloride is used as a catalyst.

Arsenic Trichloride—$AsCl_3$, m.p. −18° C., b.p. 130° C. This compound is usually prepared by the action of sulfur chloride on arsenous oxide:

$$2As_2O_3 + 6S_2Cl_2 = 4AsCl_3 + 3SO_2 + 9S$$

The trichloride is purified by distillation. It is a colorless oil, soluble in CCl_4 and most hydrocarbons.

Beryllium Chloride—$BeCl_2$, m.p. 440° C., b.p. 520° C. This chloride is prepared by chlorination of the oxide in the presence of carbon; or by the action of $COCl_2$ on the oxide at elevated temperature. $BeO + C + Cl_2 = BeCl_2 + CO$. The $BeCl_2$ sublimes out of the furnace and is condensed. Metallic beryllium[19] is made by electrolyzing the fused anhydrous chloride, and the recovered chlorine can be used for chlorinating further quantities of beryllium oxide.

Magnesium Chloride—$MgCl_2$. The method described for $BeCl_2$ is applicable except that the magnesium chloride is tapped from the furnace as a liquid. The chlorination is carried out in a shaft furnace, the lower part of which is filled with graphite granules which support the charge of granular MgO and carbon, and which serve to filter out unreacted oxide or oxychloride particles from the molten $MgCl_2$ as it drips down the shaft. Metallic magnesium is now produced on a very large scale by the electrolysis of the fused chloride.[20]

Ferrous and Ferric Chloride—*Solutions.* Iron is rapidly attacked by moist chlorine at ordinary temperatures. To make ferrous chloride, $FeCl_2$, scrap iron is placed in an acid proof tower, water is trickled over the metal, while gas is passed up the tower. As long as the solution is in contact with metallic iron, only ferrous chloride is formed. The solution from the tower is further chlorinated in acid proof tanks to form ferric chloride, $FeCl_3$. Excess gas from the second stage is used in the first stage.

Ferric chloride in solution is extensively used as a coagulant in treatment of water and sewage, and to a limited extent as an etching agent in lithography. The usual commercial strength is 40 per cent, and because of its corrosive nature, it is usually shipped in rubber lined containers and tank cars.

Anhydrous. Chlorine reacts vigorously with metallic iron at temperatures above 700° C. Ferrous chloride is readily made in a water cooled steel furnace filled with scrap iron. Once the charge has been ignited, the chlorine admitted will support combustion, and the fused $FeCl_2$ can be tapped out of the bottom of the shaft as it collects. By reducing the time of contact with the iron, and by using excess chlorine, anhydrous ferric chloride can also be produced. Anhydrous solid ferric chloride can be shipped in steel drums.

The *Comstock and Wescott Process*[21] for the recovery of sulfur from sulfide ores makes use of chlorine, ferrous chloride being an intermediate product. The Aldermac deposits of Canada consist of pyrite, pyrrhotite, and chalcopyrite. When this is chlorinated at an elevated temperature, sulfur is liberated which is condensed to a liquid:

$$FeS + Cl_2 = FeCl_2 + S$$

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[19] See Chapter 24.

[20] See Chapter 24.

[21] Can. Min. J., *59,* 181 (1938).

The ferrous chloride is then oxidized with air to regenerate the chlorine, which is used over again:

$$2FeCl_2 + O_2 = 2FeO + 2Cl_2$$

Zinc Chloride—Either in anhydrous form or in solution, $ZnCl_2$ can be prepared by the action of chlorine on metallic zinc. In the wet method, the impure zinc scrap is placed in a tower, moist chlorine is admitted at the bottom, and the concentrated solution trickles down as formed. In the dry method dry chlorine is brought in contact with molten zinc at 500° C. or above. The most successful method is to conduct the chlorination batchwise in a steel crucible lined with fire clay, and water cooled on the outside. As the $ZnCl_2$ forms, it floats as a liquid on top of the bath of fused metal, and may be tapped off from time to time. The product is blue-gray, and contains a small amount of oxide. Pure white $ZnCl_2$ is easily prepared by distillation of the crude product at 730° C.

Zinc chloride (in solution) is used in the preparation of "vulcanized fiber," which in laminated form is used extensively in the manufacture of non-metallic gears. It is also used as an impregnant for fire proofing wood, and as an ingredient of dry storage batteries.

Tin Tetrachloride—$SnCl_4$, m.p. −30.2° C., b.p. 114.1° C. Direct chlorination of tin with dry chlorine may be carried out at low temperatures, for example 100-114° C. Cast iron or steel apparatus may be used. Tin is added to a bath of the tetrachloride containing a little free sulfur, and chlorine is bubbled in. The heat of reaction boils the $SnCl_4$, which is refluxed back to the chlorinator. Traces of sulfur and sulfur chloride are subsequently removed by distillation. Tin chloride is used in the weighting of silk, and as a mordant in textile dyeing.

Tin being a comparatively valuable metal, it is necessary to recover it from scrap tinned iron. The dry tin scrap is baled into bundles of 100-200 pounds each, which are then put into a steel tank. Dry chlorine is admitted to the vessel at ordinary temperature; the tin chloride drips down as it is formed and is collected.

Silicon Tetrachloride—$SiCl_4$, m.p. −70° C., b.p. 57.8° C. This volatile liquid is prepared by passing chlorine over a mixture of 90 per cent silicon alloy, and silicon carbide, at temperatures between 500-1000° C. The furnace is a vertical shaft with a steel shell cooled by a water spray on the outside, and lined with carbon slabs on the inside. The furnace must not be run so hard that the silicon melts. The $SiCl_4$ distills off as fast as formed, and is collected in a water cooled condenser. Vent gases are scrubbed with light fuel oil, from which $SiCl_4$ is recovered by distillation.

Uses. Silicon tetrachloride vaporizes readily and gives off a thin white fume in air. Until recently the principal use was in the production of smoke clouds for military purposes. Ammonia gas is used with the $SiCl_4$ to form a dense white cloud which can be easily laid down as a curtain from naval craft. More recently, silicon tetrachloride has been used as a raw material in the preparation of ethyl silicate, $Si(OC_2H_5)_4$, and similar compounds which result from the reaction between anhydrous alcohols and $SiCl_4$. These silicates have been found useful as adhesives and protective coatings, and as agents for preparing silicic acid. $SiCl_4$, which can be shipped in steel drums, can also be used as a source of anhydrous hydrochloric acid. When decomposed with water it yields 84 per cent of its own weight of dry HCl gas.

Titanium Tetrachloride—$TiCl_4$, m.p. −30° C., b.p. 136.4° C. This liquid is prepared in a manner similar to silicon tetrachloride. The base material in this case is titanium cyanonitride, containing 70-75 per cent titanium. Unlike $SiCl_4$, it can be dissolved in acidulated water without decomposition.

Uses. Titanium tetrachloride is used in the preparation of other titanium compounds, particularly the formate, which is used in mordants and lakes in dyeing. It is used in the manufacture of iris glass and iridescent colors in the ceramic industry. The principal use for titanium tetrachloride is in developing smoke screens and clouds for military use, and for sky writing. Ammonia is sometimes added for counteracting the acidity of the smoke.

Titanium Trichloride—$TiCl_3$. This substance is made by the reduction of titanium tetrachloride with zinc, in aqueous solution. A solution of titanium trichloride is a powerful reducing agent, and it has extensive application in the textile coloring industry in stripping direct colors dyed on cotton and especially wool fabrics.

Sulfur Chloride—Sulfur monochloride, S_2Cl_2, is a lemon yellow or yellowish liquid, m.p. −80° C., b.p. 138° C. In the United States the general practice is to carry out the chlorination in large horizontal cylindrical steel tanks. Sulfur is dumped through the manhole, usually on top of a small pool of sulfur chloride left from the last chlorination, as this facilitates starting up. Dry chlorine gas is turned into the charge and the sulfur dissolves as it reacts. The charge is not permitted to warm up above about 100° C., but no special cooling is required except in the summer time.

Sulfur dichloride, SCl_2, m.p. −78° C., b.p. 59° C., is made by continuing the chlorination of sulfur monochloride. If the chlorination is carried past 65 per cent SCl_2, cooling coils must be used in the tank. When the chlorine contains much inert gas, which would volatilize the low-boiling SCl_2, reflux condensers are provided, and then scrubbers containing S_2Cl_2 to absorb excess Cl_2 and uncondensed SCl_2. Generally the sulfur contains a small amount of moisture, so that some HCl is liberated, which is scrubbed from the tail gases in a water scrubber.

Uses. Sulfur monochloride is a powerful chlorinating agent for both inorganic and organic synthesis. It is used in metallurgy and in dyestuff manufacture. Sulfur chloride is one of the raw materials for making "mustard gas,"[22] or dichlordiethylsulfide, $(Cl{\cdot}CH_2CH_2)_2S$, which is the most important military gas yet developed for chemical warfare. Dissolved in carbon bisulfide, sulfur dichloride is used in the cold vulcanization process for rubber. Formerly sulfur chloride was used on a large scale for the manufacture of acetic anhydride, the essential chemical in the manufacture of cellulose acetate. In recent years, however, direct oxidation methods have superseded the sulfur chloride method to a large extent. Sulfur chloride plays an important intermediary role in the manufacture of carbon tetrachloride.[23]

Thionyl Chloride—$SOCl_2$, m.p. −104.5° C., b.p. 78° C. This liquid is prepared by the action of chlorine on a mixture of 100 per cent H_2SO_4 and sulfur dichloride:

[22] See Chapter 33.

[23] See p. 466.

$$2H_2SO_4 + 3SCl_2 + Cl_2 \rightarrow 2SOCl_2 + 4HCl + 3SO_2$$

The $SOCl_2$ is purified by distillation.

Uses. Thionyl chloride is used in organic synthesis to replace various groups, such as OH, SH, NO_2, H, or O, with chlorine. The most important use is in the preparation of acid chlorides from organic acids. The gaseous by-products make it an easy reaction to carry out. An example is the formation of acetyl chloride:

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + HCl + SO_2$$

It is also used to prepare isoamyl chloride from isoamyl alcohol.

Sulfuryl Chloride—SO_2Cl_2, m.p. −54.1° C., b.p. 69.1° C. This liquid is prepared by direct addition of dry sulfur dioxide and chlorine gases over an active carbon catalyst in contact with water cooled walls. Steel equipment is used, and the product is condensed in a steel condenser. Sulfuryl chloride fumes strongly in moist air. With water it decomposes to form sulfuric and hydrochloric acids:

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

and it is sometimes used as a source of supply of these acids in anhydrous form.

Carbonyl Chloride—$COCl_2$, m.p. −104° C., b.p. 8.2° C. This gas, known as phosgene, is produced[24] by direct union of carbon monoxide and chlorine gases over an activated charcoal catalyst at 100-125° C. It is commercially available in liquefied form, being shipped in steel cylinders. It is very poisonous, and found extensive application in chemical warfare in 1915-1918. It is used in many organic syntheses, for example in the production of Michler's ketone, a dye intermediate. It is also a powerful chlorinating agent, and is used in metallurgy to effect separation of ores by conversion of metallic oxides to the more volatile chlorides.

Phosphorus Chlorides—Phosphorus trichloride, PCl_3, m.p. −115° C., b.p. 76° C., is made commercially in iron, nickel or bronze retorts. Phosphorus is added to the pool of PCl_3 and chlorine is blown in. As white phosphorus is generally used, an atmosphere of CO_2 is maintained in the equipment to prevent oxidation. The crude PCl_3 is purified by distillation. It is used in the production of PCl_5, and also in the synthesis of dyestuffs.

Phosphorus pentachloride is prepared by spraying PCl_3 into a steel chamber containing dry chlorine gas. PCl_5 settles out as a white crystalline powder. It sublimes at 140° C., but can be melted under pressure at 148° C. PCl_5 reacts with water to form first $POCl_3$ and then H_3PO_4.

Phosphorus oxychloride, $POCl_3$, m.p. 1.2° C., b.p. 107.2° C. This technically important compound may be made by the action of dry potassium chlorate on phosphorus trichloride:

$$3PCl_3 + KClO_3 = 3POCl_3 + KCl$$

It may also be made by the action of sulfuryl chloride on phosphorus trichloride:

$$PCl_3 + SO_2Cl_2 = POCl_3 + SOCl_2$$

although this method is not practiced at present. The oxychlorides are then separated by fractional distillation. Phosphorus oxychloride is used in organic

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[24] See also Chapter 33.

synthesis for the preparation of acid chlorides, anhydrides; in the manufacture of triphenyl methane dyes; [25] and in the manufacture of phosphoric acid esters, such as tricresyl phosphate.

Nitrogen Chlorides—Nitrogen trichloride, NCl_3, in liquid form is very dangerous, exploding on shock. It forms when chlorine comes in contact with ammonium compounds such as NH_3, NH_4Cl, either dry or in solution. Nevertheless, when carefully formed and volatilized with an air stream, it has found application in the bleaching and aging of flour. Chloramine, NH_2Cl, is also unstable to handle, yet it forms the basis of an important improvement in the sterilization of water in swimming pools, which has been widely accepted in recent years. Excess, or residual chlorine, in water above 0.5 part per million is intolerable to swimmers. Residual chlorine less than this amount is rapidly used up, especially when the pool is being used. If, however, ammonia is added with the chlorine to the water as it passes through the chlorinating equipment, the stability of the available chlorine is greatly improved, thus giving protection to swimmers in all parts of the pool for much longer periods of time. The chloramine treatment is also used in purifying drinking water, and in slime control in pulp and paper mills.

CHLORINE IN ORGANIC CHEMISTRY

Chlorine is used in large quantities in the industrial manufacture of organic compounds numbering into the hundreds. Because of its versatile nature it is used to make intermediate compounds which are further reacted to form a wide variety of products such as ethylene glycol (Prestone),[26] and phenol. It is also found in many finished compounds such as carbon tetrachloride, and paradichlorbenzene.

The principles of the unit operation of chlorination of organic compounds have been discussed previously.[27]

Compounds containing chlorine undergo reactions which allow their use to prepare other products. Chlorine may be split off by pyrolysis, leaving a double bond, as in the preparation of vinyl chloride:

$$CH_2Cl \cdot CH_2Cl \rightarrow CH_2 = CHCl + HCl$$

It may be replaced by hydroxyl, as in the preparation of phenol:

$$C_6H_5Cl + NaOH \rightarrow C_6H_5OH + NaCl$$

or by an amino group, as in the preparation of aniline:

$$C_6H_5Cl + NH_3 \rightarrow C_6H_5NH_2 + HCl$$

or by hydrogen, as in the synthesis of chloroform:

$$CCl_4 + H_2 \rightarrow CHCl_3 + HCl$$

Extent of the Industry—About 60 per cent or 270,000 tons of the 450,000 tons of chlorine produced in 1939 was consumed in making chemicals. The principal organic compound containing chlorine is carbon tetrachloride, and the

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[25] See Chapter 28.
[26] Trade name—Carbide & Carbon Chemicals Corp., New York N. Y.
[27] See Chapter 3.

90,500,000 pounds produced in 1939 required only 42,000 tons of chlorine. From these figures it can be realized that the number of products consuming chlorine must be large to account for the utilization of 270,000 tons of chlorine by the chemical industry as chemicals. For the reason that so many compounds are manufactured by the use of chlorine, only the principal ones will be described.

Character of the Reaction—The direct addition of chlorine to hydrocarbons causes a more or less uncontrollable, exothermic reaction that sometimes results in the formation of carbon and HCl equivalent to the hydrogen present in the hydrocarbon. If the reaction is so controlled that this does not happen, several compounds of chlorine and the hydrocarbon are formed in most cases. As an example, when chlorine and methane are heated together at 250° C., all four chlorine compounds of CH_4 may be formed, i.e., CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4, by the elimination of one to four atoms of hydrogen from the CH_4. The same holds true for all hydrocarbons. Most of the commercially available chlorohydrocarbons are formed under carefully controlled conditions[27] so that a preponderance of one or possibly two products results.

Frequently, elemental chlorine is not used at all, but other reactions are utilized to introduce chlorine into the hydrocarbon. For example, CCl_4 is produced by the action of sulfur monochloride (S_2Cl_2) on carbon bisulfide. Other chlorinating agents frequently used include $POCl_3$, PCl_5, $SOCl_2$, NOCl, $COCl_2$, SO_2Cl_2.

In many cases it is not possible to form the desired compound directly, and a chlorination step is followed by removal of HCl by pyrolysis, or alkali treatment. The production of trichlorethylene, C_2HCl_3, from tetrachlorethane, $C_2H_2Cl_4$, is an example of this method.

Chlorohydrocarbons as a class are excellent solvents for such purposes as dry-cleaning, degreasing oily objects, extracting oil and other materials from natural plant products. They also dissolve paints, varnishes and resins in varying degree and are used as paint removers. Special additional uses will be indicated in the description of the various compounds.

Carbon Tetrachloride—Carbon tetrachloride, CCl_4, m.p. −22.6° C., b.p. 76.8° C., is one of the most important solvents. Production in the United States in 1939 is reported[28] to be 90,500,000 pounds. It can qualify as either an inorganic or an organic compound, although at present the largest portion is made by inorganic methods. Manufacturing methods may be classified under four headings:

1. Direct chlorination of carbon bisulfide.
2. Indirect chlorination of carbon bisulfide with sulfur chloride.
3. Chlorination of methane.
4. Chlorinolysis of hydrocarbons.

Direct Chlorination of Carbon Bisulfide.[29] This process is carried out in three stages:

First stage: $2CS_2 + 6Cl_2 = 2CCl_4 + 2S_2Cl_2$
Second stage: $2S_2Cl_2 + CS_2 = 6S + CCl_4$
Third stage: $6S + 3C = 3CS_2$

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[28] United States Tariff Commission, Synthetic Organic Chemicals, 1939, Report No. 140.

[29] Niagara Smelting Corp., Niagara Falls, N. Y.

Referring to Figure 1, it is seen that in the first stage a solution of CS_2 in CCl_4 obtained from the second stage is chlorinated to produce additional CCl_4. Most of the CCl_4 is distilled off through a rectifying column, giving a product containing 99 per cent CCl_4, which is then purified by neutralization. In the second stage the S_2Cl_2, containing some CCl_4, is reacted with CS_2. The CCl_4 and most of the S_2Cl_2 produced is distilled off, leaving melted sulfur. This sulfur is then freed from S_2Cl_2 by sweeping out with air, and the recovered sulfur may be used in the third stage to produce carbon bisulfide.

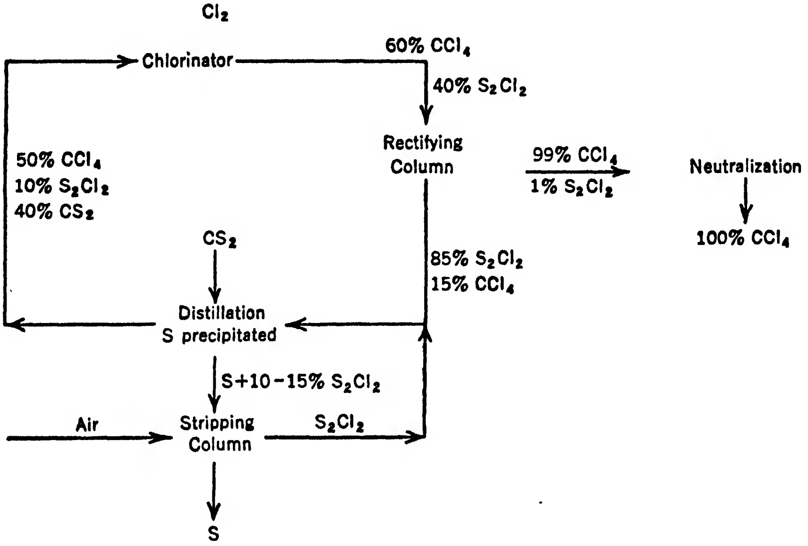

Fig. 1. Carbon Tetrachloride by Direct Chlorination of Carbon Bisulfide.

Indirect Chlorination of Carbon Bisulfide with Sulfur Chloride. This process is also carried out in three stages:

First stage: $2SCl_2 + CS_2 = CCl_4 + 4S$
$2S_2Cl_2 + CS_2 = CCl_4 + 6S$
Second stage: $4S + 2Cl_2 = 2S_2Cl_2$
$2S + 2Cl_2 = 2SCl_2$
Third stage: $C + S = CS_2$

These reactions may be either carried out batchwise[80] or continuously.[81] The chlorination of sulfur in the second stage is generally carried beyond the sulfur monochloride stage. In the first stage the CS_2 is added to the sulfur chloride under reflux conditions to take care of the heat of reaction. The crude CCl_4 that distills over contains about 0.25 per cent CS_2, and this must be removed in a purification step which consists of direct chlorination and fractional distillation.

Chlorination of Methane. Where cheap natural gas is available, methane may be chlorinated to produce any or all of the following: methyl chloride,

[80] Warner Chemical Co.
[81] Dow Chemical Co.

CH_3Cl, methylene chloride, CH_2Cl_2, chloroform, $CHCl_3$, and carbon tetrachloride, CCl_4. The reaction $CH_4 + 4Cl_2 = CCl_4 + 4HCl$ is strongly exothermic. The chief problem is to bring the gases to reacting temperature (250-400° C.) and yet to prevent the temperature from rising so high that decomposition occurs with deposition of carbon: $CH_4 + 2Cl_2 = C + 4HCl$. One of the successful methods now practiced commercially[32] is to blow the mixture of methane and chlorine through an inert molten salt bath, which can be kept at the desired temperature by cooling. Another successful method[32a] is to add the preheated chlorine gas successively through a series of jets to a high velocity stream of methane. Velocities are such as to exceed the rate of flame propagation, and thus no burning or explosions take place. The chlorination takes place in nickel tubing, and temperature is controlled by molten salt baths or other suitable means.

Chlorinolysis of Hydrocarbons. Carbon tetrachloride is obtained as a by-product from the following type reaction, which is carried out at elevated temperatures ranging from 250° C. to 425° C.:

$$C_3H_6Cl_2 + 6Cl_2 \rightarrow C_2Cl_4 + CCl_4 + 6HCl$$

Uses. Carbon tetrachloride finds wide commercial application in all processes in which a non-flammable and powerful solvent is desired. A large number of fire extinguishers contain CCl_4 as the principal ingredient of the extinguishing liquid. Usually a small amount of chloroform is added for the purpose of lowering the freezing point. Being a non-conductor, it is especially suited to combating fires around electrical equipment. It is used as a dry cleaning solvent, and for degreasing oily machine parts. It is also used in admixture with cheaper solvents, such as benzene and naphtha, for the purpose of reducing the flammability of these solvents. It finds application in the extraction of oils from press cakes and oil seeds,[33] and for degreasing[34] bones, hides and garbage.

METHANE DERIVATIVES

While methane can be chlorinated directly to the four chloromethanes, this method of conversion is only feasible where cheap methane or natural gas and cheap chlorine are available in the same locality.[35]

Methyl chloride, CH_3Cl, b.p. −23.7° C., is prepared chiefly by the action of HCl on CH_3OH in the presence of H_2SO_4. It is principally used as a refrigerant, and to some extent as an intermediate and solvent. It is of interest to note that in the early 1920's the production of methanol from methane by way of methyl chloride was proposed. Methyl chloride can be hydrolyzed by the reaction:

$$2CH_3Cl + Ca(OH)_2 \rightarrow 2CH_3OH + CaCl_2$$

This possibility was eliminated by the development of the direct synthesis from carbon monoxide and hydrogen,[36] which brought cheap methanol into the world market in 1925.

[32] McBee and Haas, Ind. Eng. Chem., *33*, 137 (1941).

[32a] McBee and Haas, ibid.

[33] See Chapter 41.

[34] See Chapter 43.

[35] Belle Alkali Co., Belle, W. Va., and Great Western Chemical Co., division of Dow Chemical Co., Pittsburg, Cal.

[36] See Chapter 30.

Methylene chloride, CH_2Cl_2, b.p. +39.8° C., can be prepared by the following methods:

1. $Cl_2 + CH_3Cl \rightarrow CH_2Cl_2 + HCl$
2. $2Cl_2 + CH_4 \rightarrow CH_2Cl_2 + 2HCl$
3. Reduction of $CHCl_3$

It is used as a refrigerant, an intermediate in organic synthesis, and as a dewaxing agent for petroleum refining. Consumption as an intermediate is small because formaldehyde, HCHO, can be utilized for most of the reactions involving methylene chloride, and it has only minor use as a solvent because better solvents are available.

Chloroform, $CHCl_3$, b.p. 61.2° C., is made by two processes:

1. $Ca(OCl)_2$ on acetone or ethyl alcohol
2. Reduction of CCl_4 with moist iron: $CCl_4 + (H) \xrightarrow[H_2O]{Fe} CHCl_3 + HCl$

The latter process is the more important and is the principal source of $CHCl_3$. Three million pounds were produced in the United States in 1939. It is used for organic synthesis, and medicinals. Its use as an anesthetic is now decreasing although at one time it was important for this purpose.

Dichloro difluoromethane, CCl_2F_2, b.p. −30° C., is made from the action of antimony trifluoride, SbF_3, on CCl_4 and is known commercially as "Freon," "F-12" and "Kinetic No. 12." It is used extensively as a refrigerant, especially in household units, for which its non-toxicity, non-corrosiveness, non-flammability, and ideal thermodynamic properties are suited.

ACETYLENE DERIVATIVES

The two-carbon chlorine compounds are very important industrially, both as products and as intermediates in the manufacture of other chemicals. A whole line of products, numbering over fifty compounds, is prepared from ethylene or acetylene by use of chlorine during the manufacturing process. The products derived from acetylene will be described first.[37]

Tetrachlorethane, acetylene tetrachloride, $CHCl_2CHCl_2$, b.p. 146° C., is prepared in large quantities by the addition reaction of chlorine and acetylene. Since the two gases may unite explosively if mixed together, they are introduced alternately into a solution of antimony pentachloride, $SbCl_5$. Acetylene is led in at a temperature of 60-80° C., and then the Cl_2 is introduced at a temperature of 80-100° C. The tetrachlorethane is recovered by distillation. Although this compound is the most powerful solvent of the chlorinated hydrocarbon series, it is used chiefly as the source of other compounds, such as trichlorethylene. It is an excellent solvent for cellulose acetate, paints, varnishes, resins, waxes, oils and fats; it is quite toxic and attacks metals in the presence of moisture.

Tetrachlorethylene, $CCl_2{=}CCl_2$, b.p. 118.5° C., is made by dehydrohalogenation (removal of HCl) of pentachlorethane with alkali. Pentachlorethane, C_2HCl_5, is a by-product of the preparation of tetrachlorethane from acetylene

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[37] For a discussion of the nomenclature see Ellis, C., "The Chemistry of Petroleum Derivatives," pp. 466–7, Reinhold Pub. Corp. (1934).

and chlorine. It also results as a by-product from the chlorination of ethyl chloride or ethylene dichloride, and from the reduction of carbon tetrachloride. The preparation of tetrachlorethylene from pentachlorethane may be illustrated by the equation:

$$CCl_3CHCl_2 + NaOH \rightarrow CCl_2{=}CCl_2 + NaCl + H_2O$$

Its chief use is as a solvent for dry cleaning where it is somewhat better than trichlorethylene, in that it does not attack cellulose acetate dyes. Its cost is higher than that of CCl_4 or trichlorethylene and therefore the latter two will not be immediately displaced by C_2Cl_4 in this field.

Trichlorethylene, $CHCl{=}CCl_2$, b.p. 87° C., is prepared by heating tetrachlorethane with an alkali to remove HCl. The reaction with lime is:

$$2CHCl_2CHCl_2 + Ca(OH)_2 \rightarrow 2CHCl{=}CCl_2 + CaCl_2 + 2H_2O$$

This compound is the most important of the chlorinated solvents; it is nonflammable, stable and non-corrosive. Because of its powerful solvent action it is used in the extraction of oils from oil seeds, in dry cleaning where it has displaced CCl_4 to some extent, in degreasing metals, textiles, and leather, and in solvent refining of petroleum. It is also an intermediate in organic synthesis.

1,2 dichlorethylene, $CHCl{=}CHCl$, is sold commercially as a mixture of its two isomers, 40 per cent of the cis form, b.p. 48° C., and 60 per cent of the trans form, b.p. 60° C., so that the b.p. of the mixture is 52-55° C. To prepare it, acetylene tetrachloride is reduced with iron and water or trichlorethylene is reduced with iron or zinc and water. The mixture may be used as a substitute for ether in many extractions where a low-boiling, non-corrosive solvent is required. It is also used as a refrigerant.[38]

1,1 dichlorethylene, $CCl_2{=}CH_2$, b.p. 31.7° C., also known as vinylidene chloride, is the raw material for a recently developed plastic with interesting properties.[39] It can be prepared by splitting HCl out of 1,1,1 trichlorethane, CCl_3CH_3, by pyrolysis or by an alkali treatment. 1,1,1 trichlorethane is made by chlorinating ethylidene chloride, $CHCl_2CH_3$, or by the action of PCl_5 on acetyl chloride.

Vinyl chloride, $CH_2{=}CHCl$, b.p. $-14°$ C., can be prepared from either ethylene or acetylene. Ethylene is first chlorinated to ethylene dichloride, CH_2ClCH_2Cl, which can then either be pyrolyzed at 400-600° C. or reacted with caustic to form vinyl chloride, $CH_2{=}CHCl$.

Recently, a plant for the manufacture of this material by the addition of hydrogen chloride to acetylene has begun production at Niagara Falls, New York.[40] Acetylene from a local carbide company is purified and mixed with anhydrous HCl manufactured by a nearby electrolytic chlorine plant. The mixed dry gases are reacted in a catalyst chamber equipped with water cooled walls placed close together in order to remove the heat of reaction. Approximately 6.74 cubic feet of C_2H_2 under standard conditions and 0.62 pounds of

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[38] Carrier Engineering Corp.

[39] Saran, made by Dow Chemical Co., Midland, Mich.
See also: Ind. Eng. Chem., News Ed., *18*, 923 (1940).
For properties of the plastic see Chapter 31.

[40] B. F. Goodrich Rubber Co.

HCl are consumed per pound of vinyl chloride produced. The vinyl chloride is liquefied and distilled at low temperature to eliminate impurities. It is stored at −25° C. in stainless steel or aluminum containers to prevent polymerization. Bronze catalyzes the polymerization. This vinyl chloride is used to produce "Koroseal."[41]

Liquid vinyl chloride polymerizes readily in the presence of certain promoters, such as benzoyl peroxide, to a white, amorphous powder. The polyvinyl chloride is mixed with a plasticizer, such as tricresyl phosphate, and kneaded in a Banbury mixer to a rubber-like plastic material which has valuable properties for many purposes. Vinylite,[42] a copolymer of vinyl chloride and vinyl acetate, $CH_3COOCH{=}CH_2$, is a plastic material that has many uses.[43] Spun into a synthetic textile fiber, it is known as Vinyon.[44] The mixture of vinyl chloride and vinyl acetate[45] can be prepared by treatment of the ethylene dichloride under pressure with sodium acetate.

ETHYLENE DERIVATIVES

Ethyl chloride, C_2H_5Cl, b.p. 12° C., can be made by passing HCl into a solution of zinc chloride and ethyl alcohol. The reaction is:

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

The addition of HCl to ethylene under anhydrous conditions in the presence of catalysts such as $AlCl_3$ or $BiCl_3$ to form C_2H_5Cl is utilized commercially. It is used as a solvent, as a local anesthetic, and as a refrigerant. However, the largest part of the production is consumed in making lead tetraethyl by reaction with lead-sodium alloys, and ethyl cellulose by reaction under pressure with alkali cellulose.

Ethylene dichloride, dichlorethane, CH_2ClCH_2Cl, b.p. 84° C., is a by-product of the production of ethylene chlorohydrin from ethylene and chlorine water. The reactions involved are the basis of a line of over fifty commercial products[46] and are worthy of explanation. The basic reaction for the series may be considered to be:

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl$$

Addition of C_2H_4 to the reactants causes three principal reactions to occur:

1. $Cl_2 + C_2H_4 \rightarrow CH_2ClCH_2Cl$ (ethylene dichloride)
2. $HCl + C_2H_4 \rightarrow C_2H_5Cl$ (ethyl chloride)
3. $HOCl + C_2H_4 \rightarrow CH_2OHCH_2Cl$ (ethylene chlorohydrin)

The second one involving HCl is very slow so very little ethyl chloride is formed, and the HOCl adds much more rapidly than Cl_2 at the low concentrations of HOCl and HCl attained by passage of chlorine into water. By controlling the concentration of ethylene chlorohydrin dissolved in the water, the formation of

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[41] See Chapter 39.
[42] Product of Carbide and Carbon Chemicals Corp.
[43] See Chapter 31.
[44] Ind. Eng. Chem., News Ed., *19,* 135 (1941).
[45] See Compound 139, Chapter 27.
[46] Carbide and Carbon Chemicals Corp., New York, N. Y.

ethylene dichloride is varied. When the concentration of CH_2OHCH_2Cl is greater than 5-10 per cent, the rate of formation of CH_2ClCH_2Cl increases.

Ethylene dichloride can also be made by reacting chlorine with ethylene either in the gas phase in the presence of diluents or catalysts, or by leading dry ethylene into liquid chlorine. It can also be prepared from ethane and chlorine by a substitution reaction.

Ethylene dichloride finds use for extraction of pyrethrins from the pyrethrum daisy, nicotine from tobacco, and fats from oil seeds; and as a fumigant. It is also used in the synthesis of other organic compounds, such as ethylene diamine,[47] and glycol monosalicylate and cinnamate. The rubber substitute, Thiokol,[48] is made from ethylene dichloride and sodium polysulfide.

Ethylene chlorohydrin, CH_2OHCH_2Cl, b.p. 132° C., is formed as described above by the addition of HOCl to ethylene. The 5-10 per cent mixture in water is distilled as a constant boiling mixture of 42 per cent in water. For most uses, this solution is suitable. Anhydrous material can be prepared by further rectification and subsequent salting out. Almost all of the ethylene chlorohydrin produced is used as an intermediate to synthesize other chemicals, such as ethylene glycol,[49] ethylene oxide, cellulose solvents, amines, carbitols, indigo, malonic acid, etc.

β,β'dichlorodiethyl ether $(CH_2ClCH_2)_2O$, b.p. 178° C., is a by-product of the action of HOCl in water on ethylene:

$$2C_2H_4 + 2HOCl \rightarrow (CH_2ClCH_2)_2O + H_2O$$

It is also formed by the simultaneous treatment of ethylene chlorohydrin with chlorine and an excess of ethylene at 80° C., followed by distillation, to give an 85 per cent yield, with ethylene dichloride as a by-product. The reaction is:

$$Cl_2 + C_2H_4 + CH_2ClCH_2\,OH \rightarrow (CH_2ClCH_2)_2O + HCl$$

The chloroether is a very good solvent and is used in the refining of petroleum by the Chlorex[50] process.[51] In 1938 about 13 per cent of the solvent refined lubricating oils in the United States was prepared by use of this chloroether.

Dichlorodiethyl sulfide, mustard gas, $\beta,\beta'(ClCH_2CH_2)_2S$, b.p. 218° C., is the important vesicant military poison gas used during the World War. It is prepared by passing ethylene into sulfur monochloride according to the equation:

$$C_2H_4 + S_2Cl_2 \rightarrow S + S\,(CH_2CH_2Cl)_2$$

For a description of the process, see Chapter 33.

PROPYLENE DERIVATIVES

The three carbon chlorine compounds derived by the chlorination of propane and propylene from cracking still gases are being developed.[52] Probably the most important result of this work is the synthetic glycerine process based upon the

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[47] See Compound 22, Chapter 27.
[48] Thiokol Corp. Also see Chapter 39.
[49] Prestone, trade name Carbide & Carbon Chemicals Corp. See also Chapter 30
[50] Chlorex, trade name, Carbide & Carbon Chemicals Corp.
[51] Developed by Standard Oil Co. (Indiana). See also Chapter 14.
[52] Shell Chemical Co., San Francisco, Cal.

chlorination of propylene.[53] This process very definitely fixes the maximum price of glycerine from any source to that price which can be realized by chemical methods, and has undoubtedly been responsible for the stable price of this basic explosives raw material during the second World War. Stabilization of the price of glycerine should also stimulate expansion of other industrial utilizations of glycerine as in the manufacture of ester gum and alkyd resins.[54]

The synthetic glycerine process will be briefly outlined. Reactions involved are shown by the equations:

$$CH_2{=}CHCH_3 + Cl_2 \xrightarrow{500^\circ\text{ C.}} CH_2{=}CHCH_2Cl + HCl \qquad (1)$$

$$\underset{\text{(allyl chloride)}}{CH_2{=}CHCH_2Cl} + NaOH \rightarrow \underset{\text{(allyl alcohol)}}{CH_2{=}CHCH_2OH} + NaCl \qquad (2)$$

$$CH_2{=}CHCH_2OH + HOCl \rightarrow CH_2OHCHClCH_2OH\ \text{(monochlorohydrin)} \qquad (3)$$

$$CH_2OHCHClCH_2OH + NaOH \rightarrow \underset{\text{(glycerine)}}{CH_2OHCHOHCH_2OH} + NaCl \qquad (4)$$

Direct chlorination of propylene at 500° C., so-called "hot chlorination," results in a substitution reaction to form allyl chloride by reaction (1). The yield is about 80 per cent when a 5 to 1 ratio of propylene to chlorine is used. The propylene is preheated to 400° C., and the Cl_2 is introduced through efficient mixing jets into the propylene stream in a steel tube.

The next step is the hydrolysis of the allyl chloride to allyl alcohol. A solution of sodium carbonate and sodium hydroxide is used in an autoclave, at a pH of 8-11 and a temperature of about 150° C., to give a 95 per cent yield of allyl alcohol. The third step is the chlorohydrination of allyl alcohol in water solution with chlorine at 14° C. by passing gaseous chlorine up through a packed tower while the water-alcohol solution descends over the packing.

The fourth step is the hydrolysis of the chlorohydrin, $CH_2OH{-}CHCl{-}CH_2OH$, with an aqueous solution of 10 per cent NaOH and 1 per cent Na_2CO_3 in an autoclave to give glycerine. The crude product is purified by distillation, extraction with xylene, and redistillation in vacuum. Overall yield of glycerine from allyl chloride is about 90 per cent. Possible by-products are many and can include dichloropropene, $CHCl{=}CHCH_2Cl$; dichloropropane, $CH_2ClCHClCH_3$; 2-chloropropene, $CH{=}CClCH_3$; diallyl ether, $(CH_2{=}CHCH_2)_2O$; trichloropropane, $CH_2ClCHClCH_2Cl$; epichlorohydrin, $CH_2Cl\underset{\diagdown O \diagup}{CHCH_2}$; and glycidol, $CH_2OH\underset{\diagdown O \diagup}{CHCH_2}$ among others. It is probable that the treatment of propylene and propane with chlorine will result in the development of a series of products similar to those resulting from the chlorination of ethylene.

BUTYL AND AMYL DERIVATIVES

The four and five carbon hydrocarbons are chlorinated with elemental chlorine to give a series of chloro-compounds which are valuable as intermediates.

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[53] Chem. & Met. Eng., *47*, 834 (1940).
Williams, C. E., Trans. Am. Inst. Chem. Eng., *37* (1941).

[54] See Chapter 31.

Normal and iso-pentane are commercially chlorinated in an iron tube at about 260° C. by passing chlorine and an excess of the pentanes rapidly through the tube. All of the Cl_2 reacts to give a mixture of isomeric monochlorides and some higher chlorides. The chlorides are in turn hydrolyzed to form a series of amyl compounds, such as the alcohols and acetates, which are widely used as solvents.[55]

A recent review gives 65 references to work done in the past four years alone in the field of hydrocarbon chlorination.[56] Processes and products are many and varied and no attempt can be made here to cover them all except to refer to the wide application of chlorine in this field.

The synthetic rubber, Neoprene,[57, 58] is made by two steps, as shown by equations:

$$2C_2H_2 \xrightarrow{\text{catalysts}} CH{\equiv}C{-}CH{=}CH_2 \text{ (vinyl acetylene)}$$

$$CH{\equiv}C{-}CH{=}CH_2 + HCl \rightarrow CH_2{=}CClCH{=}CH_2$$

The latter is 2-chlorobutadiene or chloroprene, which undergoes polymerization to yield synthetic rubbers.

The important synthetic rubber intermediate, **butadiene,** $CH_2{=}CH{-}CH{=}CH_2$, can be prepared by removing two molecules of HCl from dichlorobutane: $CH_2ClCH_2CH_2CH_2Cl \rightarrow 2HCl + CH_2{=}CHCH{=}CH_2$. Dichlorobutane is obtained by the chlorination of butane or butylene by several methods.

HIGHER HYDROCARBON DERIVATIVES

Chlorinated rubber,[59] used in many paints, varnishes, plastics, etc., is made by the addition of Cl_2 to a solution of rubber in a solvent such as CCl_4.

Chlorinated paraffin wax is treated with aromatic hydrocarbons and $AlCl_3$ to give complex materials such as Paraflow[60] to be added to lubricating oils as pour-point depressors, or wax crystallization inhibitors. These materials are also used in the preparation of high pressure lubricants. The addition of 0.5-0.75 per cent of the depressor will lower the pour-point of a lubricating oil 30° F., an important development for good automobile performance in the winter.

BENZENE DERIVATIVES

Chlorine compounds of the aromatic type are widely used as intermediates in the dye and pharmaceutical industries. Chlorination of ring hydrocarbons results in isomers and by-products, and avoidance of these in the production of any specific compound is often a great problem. However, the difficulties are less than in the aliphatic applications of chlorine. The most important chlorine derivatives are those of benzene and toluene. Chlorination of the ring is facilitated by the presence of a chlorine carrier like iodine and ferric chloride. Chlorination of a side chain is accomplished in the presence of light and absence of chlorine carriers.

Chlorbenzene, phenyl chloride, C_6H_5Cl, b.p. 132° C., is produced in large quantities by the direct chlorination of benzene in the presence of a catalyst such

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[55] Chem. & Met. Eng., *47*, 493 (1940).

[56] Ind. Eng. Chem., *33*, 137 (1941).

[57] E. I. du Pont de Nemours & Co.

[58] See Chapter 39.

[59] See Chapter 39.

[60] Standard Oil Co. of New Jersey.

as molybdenum chloride, aluminum-mercury couple, ferric chloride, or antimony trichloride mixed with silicon and lead. The reaction proceeds according to the following equation:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

The HCl formed passes off as a gas to be recovered as hydrochloric acid by absorption in water. A yield of about 70 per cent is realized. Some of the HCl remains dissolved in the crude chlorbenzene and this is neutralized by washing with NaOH solution. The crude chlorbenzene is then rectified by fractional distillation, and the by-products recovered are chiefly the ortho and para dichlorbenzenes and unreacted benzene. Chlorination of benzene may also be carried out in the vapor phase method in the presence of catalysts (such as a Deacon process catalyst, $CuCl_2$ deposited on clay or pumice) at 200-400° C. Most of the chlorbenzene produced is consumed in the preparation of synthetic phenol and aniline.

Phenol—A very large portion of the phenol, C_6H_5OH, produced[61] in the United States is now made synthetically by the chlorination method in two stages:

$$C_6H_6 \rightarrow C_6H_5Cl \rightarrow C_6H_5OH$$

The hydrolysis of chlorbenzene is accomplished either by means of alkali or by steam. The Dow process utilizes the alkaline method whereby chlorbenzene, 25 per cent excess Na_2CO_3, and water are reacted continuously at 3000 pounds per square inch and 320-400° C., to give a 90 per cent or better yield of phenol. There is also formed a by-product, diphenyl oxide, which is used in perfumery because of its geranium odor, and which is a component of Dowtherm,[62] a high temperature heating medium.

In 1940 a plant was built to manufacture 15,000,000 pounds of phenol per year by the catalytic conversion of benzene to phenol by the **Raschig process,**[63] which is regenerative with respect to chlorine.

The conversion of benzene to phenol is carried out catalytically in the vapor phase in two stages. Benzene is chlorinated with HCl and air over a catalyst in the first operation at 230° C. by the exothermic reaction:

$$C_6H_6 + HCl + \frac{1}{2}O_2 \rightarrow C_6H_5Cl + H_2O$$

About 10 per cent per pass is converted to chlorbenzene, and continuous fractional condensation separates the C_6H_5Cl so that the unreacted gases may be recirculated. The second stage is endothermic and is carried out at 425° C. by the reaction represented by the equation:

$$C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$$

Here, too, the conversion is only 10 per cent. The HCl, H_2O and phenol are condensed from the chlorbenzene vapor and then the phenol is extracted from the acid with benzene. The HCl is distilled off of the water solution and re-

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[61] For the production from coal tar see Chapter 16.

[62] Dow Chemical Co., Midland, Mich.

[63] Durez Plastics and Chemicals, Inc.
See Ind. Eng. Chem., News Ed., *18,* 921 (1940), and Chem. & Met. Eng., *47,* 770-5 (1940).

turned to the first stage. The phenol is separated from the benzene by distillation and the benzene is returned to the first stage. Only 0.1 pound of by-products (polychlorbenzenes and diphenyl compounds) is produced per pound of phenol made. The HCl operating efficiency is 97 per cent.

This process has been used in Germany successfully and the efficient operation of this first United States plant indicates that other installations will be made in this country as the demand for phenol increases with the expansion of the phenolic resin industry.[64]

Chlorbenzene is also used to prepare aniline,[65] picric acid,[66] dinitrochlorbenzene, and various dyes. Three million five hundred pounds of chlorbenzene were sold as such in 1939 in the United States.

Dichlorbenzenes, ortho and para, are produced in a ratio of about three pounds of para per pound of ortho by the further chlorination of chlorbenzene. Para dichlorbenzene is a solid which volatilizes at room temperature, m.p. 53° C., b.p. 173.7° C.; and ortho dichlorbenzene is a liquid, b.p. 179° C. The para form is consumed in large quantities as a household moth-preventative, and has replaced to a great extent the "moth-balls" made of naphthalene. It is also used as a fumigant, germicide and deodorant. The ortho isomer is used as a solvent and paint preservative. Both forms are used in organic synthesis. The 1939 domestic production was 5,000,000 pounds of ortho and 15,800,000 pounds of para.

Pentachlorphenol, $C_6(OH)Cl_5$, is a valuable wood preservative and fungicide, and is used in paper mills to prevent slime formation in the "white water." It is made by the chlorination of phenol in the presence of a chlorine carrier such as aluminum chloride.

2,4-dinitrochlorbenzene, m.p. 37-53° C., is obtained by nitrating chlorbenzene first to ortho and para nitrochlorbenzene. Upon further nitration both yield the 2,4-dinitro compound, which is an important intermediate for the preparation of various sulfur dyes and picric acid. The latter is obtained by first hydrolyzing the 2,4-dinitrochlorbenzene to dinitrophenol and then adding the third nitro group to give picric acid, $C_6H_2(NO_2)_3OH$. Seven million five hundred pounds of dinitrochlorbenzene were produced in the United States in 1939.

TOLUENE DERIVATIVES

Chlorination of toluene is carried out by passing chlorine into boiling toluene. The typical chlorinating vessel is lead or glass lined, and it is internally illuminated with powerful electric lights. Three products are made successively, although overlappingly, and these compounds are readily hydrolyzed with alkali.

The principal products are: benzyl chloride,[67] $C_6H_5CH_2Cl$, benzal chloride,[68] $C_6H_5CHCl_2$, benzotrichloride,[69] $C_6H_5CCl_3$ and benzoyl chloride,[70] C_6H_5COCl.

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[64] For the use in the plastic field see Chapter 31.

[65] See Chapter 28.

[66] See Chapter 32.

[67] See Compound 192, Chapter 27.

[68] See Compound 176, Chapter 27.

[69] See Compound 186, Chapter 27.

[70] See Compound 188, Chapter 27.

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CHAPTER 12

ELECTROCHEMICAL INDUSTRIES

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The modern chemical plant has followed the engineering practice of most other industries and extensively utilizes electric energy for driving its equipment, for lighting, for signaling and communication, for measurement and indication. Such uses of the electric current are not within the scope of this chapter. We shall concern ourselves here only with those applications of electric energy as bring about or promote the specific chemical reactions upon which our processes are founded.

The more important of the electrochemical industries are of comparatively young age, possibly some sixty years old, and most of them have entered fields originally developed along strictly chemical lines. Electricity thus became a new reagent destined to revolutionize an older existing art, and today one often finds direct competition between the electrochemical and the purely chemical processes. Hydrogen from the electrolytic cell is competing with this same gas produced by the water-gas steam reaction. Electrolytic caustic soda competes with the Solvay process alkali. Electrolytic zinc competes with spelter from the older retort process. In some cases the original chemical or metallurgical process has been so completely displaced by the electrochemical that there are no competitive examples existent.

Again, new industries have been built around the electrolytic cell and the electric furnace; examples in which there could be no possible comparable competitive operation that merits consideration. Without the electric furnace we could not have our modern artificial abrasive industry. Calcium carbide would have remained a laboratory curiosity; aluminum a rare metal.

THE ELECTROCHEMICAL REVOLUTION

The electrochemical process has completely revolutionized the production of certain primary products and at such lowered cost as to permit the development of new secondary industries utilizing these cheaper raw materials. Chlorine from the electrochemical cell costs about one-third that produced by the best of the older chemical processes. This has enormously encouraged the utilization of chlorine in directions that would not have been possible if we were still dependent upon the older non-electrical processes. Metallic sodium may be produced electrolytically at a cost of less than one-tenth that of the old retort method, and this cheap reagent has changed completely the character of development of a multitude of secondary industries.

Power Costs—In the group of industries we are dealing with here, the electrical energy must be looked upon as a raw material or reagent capable of promoting certain types of reaction, and in the economic analysis of any project the cost of this energy must be treated exactly the same as any other item of raw material. If the energy consumption is relatively large in proportion to the total costs, that type of industry locates at centers of cheap and plentiful power. If the electrical consumption is relatively small in comparison to total cost, then other factors determine location, and power supply is provided in the most economical manner under the existing conditions. Thus we find centers of electrochemical activity near large hydroelectric projects which can afford to sell power cheaply, and also at the same time we find similar centers located where fuel is cheap and water available, since steam power for certain typical electrochemical loads may also be produced at sufficiently low cost. On the other hand there are many electrochemical industries located where other raw materials are more important than the cost of power. For example the Niagara district once afforded large quantities of cheap power and attracted a wide variety of electrochemical industries. Carbide, ferroalloys, abrasives, chlorine and caustic plants located in this territory because of the cheap and abundant supply of electric energy. There was only one relatively small copper refinery in the district because in this operation electric power is not a controlling factor. Several large refineries are located around New York Harbor and Baltimore, for transportation plays more part in their over-all economic operation than does the difference in the cost of electric energy. Electrolytic alkali plants are widely scattered over the United States principally in regions where cheap salt is available. There are almost no electric steel furnaces in the Niagara district and yet there are a thousand operating in the country and in most widely scattered districts from New England to the Pacific coast, for in the steel melting furnace electric power is usually not a controlling factor.

The electrochemical industries are highly developed in Norway where hydroelectric power is produced as cheaply as anywhere in the world. On the other hand in Germany these industries are centering in Saxony and Southern Prussia where energy is derived from steam plants burning very cheap lignites and brown coals. It, therefore, is not possible to set down any hard and fast rule for the location of any unit in the electrochemical field and each particular division of the industry requires an independent analysis based upon a multitude of factors of which electric energy is only one.

Then again there have been remarkable improvements in the steam power plant.[1] At the time Niagara was experiencing its most rapid electrochemical development, the typical steam unit was relatively small, a few thousand kilowatts, and was consuming some 3 to 4 pounds of coal per kilowatt hour. Today we have steam generating units of more than 150,000 kilowatts per unit and fuel consumptions of less than 1 pound of coal per kilowatt hour, and the end is not yet in sight. Considering overall costs it is now possible to produce steam power in many regions of the United States cheaper than hydroelectric power can be developed. This has greatly extended the territory open to electrochemical

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[1] Gebhardt, G. F., "Steam Power Plant Engineering," John Wiley & Sons (1925); Creager, W. P., and Justin, J. D., "Hydro-electric Handbook," John Wiley & Sons (1927).

development and today there is more expansion in electrochemical facilities on the Gulf coast, based upon steam power with cheap natural gas fuel, than is taking place at Niagara, particularly as competition has forced up the price of Niagara power through the development of longer distance transmission and widespread public service distribution.

In general the electrochemical industries offer to power plants a very high load factor, 95 per cent in case of the more highly developed industry. This type of load lends itself most excellently to steam power. The hydroelectric unit is more especially adapted to public service distribution where the load factor rarely exceeds 50 per cent. During the off-peak load period water can be stored behind the dam thus increasing the peak supply. Also many of the electrochemical processes are large users of steam. With the modern bleeder-turbine these steam requirements can be met most effectively by the production of steam at high pressure and the use of the turbine as an expansion valve. In this way very great economy in either power or steam cost can be realized. Where a well-balanced unit can be installed some surprisingly low power costs are obtainable from such combination.

Where the electrochemical operation can be carried out intermittently, as for example, in the steel foundry operating on a single shift, it is possible to obtain power at extremely low rates from the local utility, provided the melting down period is scheduled at those hours of low service load. This has permitted the very wide extension of the electric melting furnace throughout the Eastern United States.

CLASSIFICATION OF ELECTROCHEMICAL INDUSTRIES

There are two major classes of this industry—

1—Electrolytic
2—Electrothermal

In the electrolytic processes the electric current produces a breaking down or chemical decomposition, the products of which may have commercial value of themselves, or in turn through secondary reactions to be converted into valuable products. This is a direct application of electrical energy to instituting a chemical reaction.

In the electrothermic processes the electric energy is converted into heat through the agency of which chemical reactions are brought about. Since enormous quantities of electric energy can be converted into heat in systems of relatively low heat capacity we can thus obtain extremely high temperatures. Such temperatures are under close control by virtue of the ease of manipulation of the electric current. Also of great advantage is the fact that there are no contaminating products of combustion.

There are important cases in which the electric current is also used for both its electrolytic and its electrothermic effect.

Sources of Current—The electrolytic process requires a source of direct current. This may be produced from batteries, though this is most uneconomical except on an extremely small scale. Direct current generators driven by prime movers were frequently a source of such current in early days of the industry, but they too have practically disappeared since such units are cumbersome, of relatively low capacity and, therefore, very inefficient. They are still found in a few of the older plants but are gradually being displaced by other equipment described below.

Modern generating equipment is of the multi-phase alternating current type. Distribution lines of any length are always supplied with alternating current.[2] Therefore, in these modern times the electro-chemist is practically restricted, both to large scale generation equipment or to connection with existing transmission lines to accept alternating current even though his processes may force the use of direct current. The electro-chemist, therefore, may expect to receive his electric energy in alternating form and at a more or less high voltage. For conversion of such to direct current he has the choice of several types of apparatus.

Direct current generators are limited by construction difficulties to currents of 20,000 amperes, and to preferred voltages not exceeding 600. The maintenance of commutators restricts us to magnitudes such as indicated and if greater amperage is required such machines are connected in multiple. Such generators may be driven by any prime mover, either steam engine or electric motor. Most commonly because of the relatively small size of these machines, they are motor driven and frequently with the motor in the middle and a generator on either side, if more than one unit is required. Such sets permit of wide regulation of the direct current output, and while the efficiency of the combination plus the transformer delivering the current to the motor rarely exceeds 90 per cent, such is the preferred type of unit in many installations.

A somewhat similar device which combines the motor and generator in a single unit is the rotary converter.[3] This unit, however, has the disadvantage that regulation of the direct current is limited to 2½ per cent either side of the designed voltage, which may be an undesirable handicap in many industries.

The most modern of the devices for converting alternating into direct current is the so-called rectifier. There are two types of this apparatus in general use with details modified by the several manufacturers. The most common of this class is the mercury rectifier[4] now available in capacities up to 8,000 kilowatts producing direct current of 10,000 amperes at 800 volts. This apparatus has no moving parts and operates at very high efficiencies in the upper ranges of voltages. It is much less expensive to install than either the rotary converter or the motor generator set, requires relatively little attention and is a sturdy piece of apparatus. It has a very considerable range of regulation in the more elaborate types.

Another kind of rectifier, known as the copper-copper oxide type, is now available in units with outputs up to 12,000 amperes, usually 6 or 12 volts e.m.f. At the present time these units lack the flexibility of the mercury type, but that is a feature that probably will be overcome as development proceeds. This also has no moving parts, and should have a long life, requiring very little attention.

There are several unique sources of direct current available to the electrochemist. The uni-polar generator, usually motor driven, is now built to operate at currents of 50,000 amperes and voltages up to 12. This compact apparatus

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[2] Still, A., "Electric Power Transmission," McGraw-Hill Book Co. (1927).

[3] Slichter, W. I., "Handbook for Electrical Engineers: Rotary Converters," John Wiley & Sons (1936).

[4] Marti, O. K., and Winograde, H., "Mercury Arc Power Rectifiers," McGraw-Hill Book Co. (1930).

furnishes extraordinarily heavy currents but at relatively low voltage and finds service where a single electrolytic cell takes care of the chemical operation.

The vacuum tube may be adapted to rectification and for practically any reasonable voltage. The current output is very small even in the larger units, but the fact that very high voltages are available through this apparatus makes it of some interest to the electro-chemist.

In the electrothermic branch of our industry alternating current is universally used. Since this is the type of current produced by all large power stations and is distributed over wide areas, the only conversion to be considered is that to a suitable voltage. For this purpose transformers are used. In electric furnace work we are called upon to handle very large currents, sometimes of the order of 60,000 amperes and upwards. The voltages are rarely above 200 and 250 volts and very frequently do not exceed 100 volts. Transformers must be specially built for this service and are always provided with some means of changing or regulating the output voltage.

Certain types of electrolytic work operate with fused baths. Direct current must be used for the electrolytic decomposition. If the units are large and efficiently designed the heating effect of this electrolyzing current may be sufficient to keep the bath molten. We do have examples, however, where the heating effect of the electrolyzing current is not sufficient to maintain the bath at the proper temperature, and it is then customary to superimpose alternating current to assist in maintaining the desired temperature.

There are also electrolytic operations which take place at ordinary temperatures that use superimposed alternating current on the direct current electrolyzing circuit. In this case the alternating current and direct current generators are specifically designed to be connected in series.

To avoid influence of electrodes it is practicable to construct furnaces on the transformer principle. A hearth of annular type loops a magnetic circuit, magnetism being induced by a high tension coil fed by alternating current. Current is induced in the molten bath in the hearth and heats the same by resistance. This induction type of furnace has found its principal application in the steel industry.

A modified form of this induction furnace is the high frequency type. High frequency current generated by transformers, condensers and spark gap, or by special generators, is passed through a coil of suitable design inside of which is placed the material to be heated. It is necessary that the crucible holding the material, or the material itself, be a relatively good conductor. The eddy currents induced in this conductor heat the same. Regulation is very easy and very high temperatures are possible in such units but they are of relatively small capacity as compared to the giant furnaces found in the carbide, ferro-alloy and steel industries, a limitation imposed by available high frequency generating equipment.

INDUSTRIAL APPLICATIONS OF ELECTROCHEMISTRY

In presenting the material which follows it is assumed that the reader has a knowledge of the fundamentals of electrochemistry. If this is not the case, he can consult some of the material dealing with the fundamentals given in the reading list at the end of this chapter.

In the necessarily brief description of the many applications of electrochemistry in our industrial economy, no attempt will be made to group them into electrolytic and electrothermal industries. The order chosen while generally based on importance, actually has much of the historical background as a basis.

Caustic Soda and Chlorine—By far the most important electrochemical process at the present time is the production of caustic soda, chlorine, hypochlorite and chlorate from common salt. These materials are covered in Chapters 10 and 11.

Oxygen and Hydrogen—A very considerable industry has grown up around the electrolytic production of the two gases oxygen and hydrogen.[5] Where essentially pure gases are demanded the electrolytic method of producing them has as yet found no competitor, particularly if both are demanded, since they are produced simultaneously by the electrolytic decomposition of water. The fractionating of liquid air for the production of oxygen in general will produce this gas at a lower cost than the electrolytic process, but its purity rarely exceeds 99.6 per cent, whereas the electrolytic oxygen can be obtained with impurities not to exceed 0.1 per cent. In such electrolytic production of oxygen, hydrogen is also obtained of a purity exceeding 99.9 per cent. Where both gases can be used, costs of production by the electrolytic method compare favorably with any other source in localities where power is relatively cheap.

The electrolytic production of hydrogen on an enormous scale is practiced in many countries producing synthetic ammonia, particularly where electric power is cheap and coke relatively costly.

There are two general types of cell construction, the choice depending upon the cost of electric energy. Where this is cheap a low cost type of cell construction of low energy efficiency is usually chosen. Where electric energy is relatively more expensive high energy efficiency cells are chosen even though they represent a material increase in capital cost over the low efficiency type.

In general, the low efficiency cell is of the unit type construction, that is, it consists of a single anode suspended in the center of a closed iron box, the sides of the box acting as cathodes. Between the anode and the cathode is a porous asbestos diaphragm which keeps separate the gases produced at the two electrodes. The anode itself is of iron usually in the form of a grid-like structure so as to permit free access of the electrolyte, and by suitable spacing permits easy evolution of the oxygen. Nickel and nickel-plated anodes are sometimes used, resulting in a slightly increased efficiency of the cell. The electrolyte is a solution of caustic potash in water. Additions of fresh water are required to make up that lost through decomposition and this water is preferably distilled to prevent accumulation of foreign salts in the cell, particularly in the mesh of the diaphragm. Many cell plants operate on raw water for a long time without disturbance, but this must be water of exceptional purity, otherwise the electrodes will be coated and the diaphragm blocked by precipitation.

Low efficiency cells operate with a voltage drop of 2.25 to 2.50 volts across the electrodes. Theoretically only 1.69 volts is required for the decomposition of water so that the energy efficiency of this type of cell is only from 68 to 75 per

[5] Taylor, H. S., "Industrial Hydrogen," Chem. Catalog Co. (1921).

cent. The current efficiencies of any modern cell are usually very high, frequently showing 98 per cent.

The high efficiency type of cell, using a voltage of 1.85 to 2 volts across the electrodes, shows better overall economy where power costs are high. This type of cell uses electrodes much more closely spaced and of a more elaborate design to allow the largest amount of effective surface and to eliminate gas bubbles as rapidly as possible from those portions of the electrolyte which lie directly in the path of the current between the two electrodes. The anodes of this type of cell are usually of nickel or of nickel-plated iron. These cells run at a much lower current density per unit of electrode and cost more to build, so for a given output the investment is somewhat greater than for the low efficiency type.

It will be noted that these hydrogen cells of either class are of low voltage, requiring only from 2 to 2.5 volts over the cell. A current of 1,000 amperes passing through such a cell produces 15.5 cubic feet of hydrogen and half as much oxygen per hour. In order to get the enormous quantities of hydrogen needed by the synthetic ammonia process, it is necessary first to use currents of high amperage.

For purposes of economy, the electrical machines should operate at the highest possible voltage. It requires about 1 sq. in. of copper conductor for each 1,000 amperes carried, so any attempt at paralleling these large machines gets into complications with the current leads. The most advanced practice has standardized at 10,000 amperes at 600 volts per circuit. In order to circumvent multiplicity of units and connections, attempts have been made to build hydrogen cells of a multiple type. In general, they are built up like a filter press with a diaphragm taking the place of the filter cloth and acting at the same time as an insulator between adjacent sections. The electrode occupies the position of the plate in the filter press, one side of it acting as a cathode and the other side as an anode. By this means, cells can be built up in a unit, so that between the end connections the drop in voltage will be from 100 to 200 volts, depending upon the number of sections clamped together, and thus simplify electrical installation. Cells of this type carrying several thousand amperes have been developed for producing hydrogen for the making of synthetic ammonia. On account of the complications in insulation and the difficulty with diaphragms, they are not in such general use as the unit type cells described above. Their installation, however, is quite simple with respect to the take-off of gases, the feeding of water and electrical connections.[6]

Calcium Carbide—When lime and carbon are mixed together in proper proportions and the mixture heated to an extremely high temperature the lime is reduced and the metallic calcium unites with the excess of carbon present to form the carbide, CaC_2. In general, the electric arc is used as the source of heat, though resistance systems have been more or less successfully employed. The reaction which takes place in the furnace is:

$$CaO + 3C = CaC_2 + CO$$

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[6] For the production of hydrogen by the producer gas reaction see Chapter 19, Industrial Gases.

This reaction would require a mixture of 875 parts by weight of lime to 563 parts of carbon per 1,000 of commercial carbide, though in actual practice the proportion of carbon used for the above quantity of lime sometimes rises as high as 650 parts, the excess being consumed in other ways than by the above reaction.

Types of Carbide Furnaces. The original carbide furnace consisted merely of a basin into which was dipped two electrodes between which an arc was sprung, the reacting mixture being fed directly into the arc. The melting-point of the carbide is in the neighborhood of 1,800° C., and so the mass sets almost as fast as formed. When the basin was full of set carbide the whole was removed from under the electrodes, allowed to cool and the carbide dug out. The operation was thus an intermittent one, and rather low energy efficiency was attained. A continuous mechanical furnace later replaced this primitive type.

FIG. 1. Calcium Carbide Furnace. (Courtesy North American Cyanamid, Limited)

Modern carbide furnaces may be either single-phase or three-phase. In general, the single-phase furnace is of relatively small productive capacity, rarely exceeding 15,000 kilowatts in power rating. The late designs have closed top through which the single electrode is sealed by suitably packed joint. This enables the collection of the gases produced in the furnace, largely carbon monoxide, and after cleaning from dust and fume this gas can be used either as a source of heat through combustion, or as a chemical reagent for conversion into ammonia, alcohol, etc.

Most of the carbide furnaces are of the three-phase type, that is, have three electrodes each connected to one of the low tension bus-bars. Such furnaces are now in operation at power ratings up to 40,000 H.P. The box or hearth is rectangular in section and built of heavy steel plate braced with structural members. The bottom is built up of a layer of refractory on top of which is a deep bed of carbon. This may be composed of large baked electrodes laid up in tar or pitch on top of which is a composite of fine coke and pitch rammed in hot, or the whole of the carbon may be of the tamped type. These carbon bottoms are many feet thick, for the temperatures in the carbide furnace run well above 2,000° C. and carbon is the only form of refractory that withstands the high temperature and the corrosive action of the furnace charge, which is quite basic in character. The side walls are usually carried up of relatively thin refractory, a practical construction where ample dimensions are given to the furnace box, for the furnace itself creates its own lining out of the semi-fused raw materials.

The electrodes for the carbide furnace are of two general types. They may be of pre-formed and baked carbon, round in the smaller furnaces and square to rectangular in the larger furnaces. In this latter case a number of the individual blocks are assembled together into a single electrode, the largest running about 24 inches wide and 120 inches in length. When such electrode is consumed the carrying head with the butt is removed from the furnace and a new electrode replaced. With proper design of detail such change is made in less than 10 minutes.

In more recent years a continuous type of electrode has appeared in the industry. These electrodes are round or oval in cross-section and are actually made and baked above and in the furnace itself. A clamping sleeve of bronze and copper brings the current to the actual electrode. In this sleeve is placed a cylindrical casing of very light sheet-iron, built up section by section through to a working floor above the hearth of the furnace. On this working floor an electrode mixture of coke and pitch is prepared and this is tamped into the cylindrical casing. As the electrode is consumed below it is slipped through the holder by loosening a wedge-like construction and new sections of casing are spot-welded to the old, and again tamped with the electrode mixture. The heat of the furnace bakes this mass into a solid electrode and in this type of furnace it is only necessary to interrupt the current in the larger sizes for a minute or so to permit the slippage of the electrode.

Most of the modern carbide furnaces operate on constant voltage. Transformers and their connections are arranged to deliver energy at a given voltage to the bus-bars leading to the furnace. In order, therefore, to maintain a constant energy in the furnace its resistance is changed by raising or lowering the electrodes. This is accomplished automatically. By means of current transformers on the main bus-bars and suitable relays, motors are controlled, which automatically raise or lower the electrode thus maintaining a relatively constant current through each electrode and this with the constant voltage furnished by the transformers gives a constant power on the furnace itself.

There are carbide furnaces in operation in which regulation of energy is accomplished through a change of voltage in the supply line to the furnace. Transformer systems are available which permit switching of the connections automatically under load and this coupled with automatic regulating transformers enables almost infinite change in the voltage supply to the furnace.

The operating voltage of a carbide furnace depends upon its design. Single-phase furnaces operate at around 60 volts between the electrode and the carbon bottom of the furnace. In the three-phase types the voltages may vary from

100 up to 200 volts between electrodes, this variation being dependent upon the size of the furnace. The usual commercial grade of carbide consumes about 3,000 K.W.H. per ton in the modern furnace.

In the small furnaces carbide is tapped intermittently from one-half to one hour intervals. In furnaces above 20,000 H.P. the tapping is practically continuous. The molten carbide is run into pans or to continuous cooling conveyors of several types and after cooling is sent to the crushing plant for sizing. Most countries in the world have a standard for commercial carbide of 85 per cent purity, that is 85 per cent CaC_2. The standard, however, is rarely expressed in this form, but more often in the metric countries in terms of liters of acetylene per kilogram of actual carbide. In English speaking countries this is cubic feet of acetylene per pound of actual carbide. Thus an 85 per cent carbide corresponds to 296 liters per kilogram or 4.75 cubic feet per pound.

Calcium carbide is used chiefly to form acetylene, and it is this use which makes it important industrially. It is also used as the starting point of cyanamid manufacture in one of the several methods used in fixing atmospheric nitrogen.[7]

ARTIFICIAL ABRASIVES

Fused Alumina—One of the early developments of the electrochemical industry and belonging to the electrothermic branch is the production of artificial abrasives. The first such product was silicon carbide, which will be described below. This material, however, while extremely hard and possessing many excellent cutting properties, is very brittle and for many purposes did not prove a wholly satisfactory substitute for the natural emery. Attempts, therefore, have been made to produce an artificial crystalline alumina or corundum and today this synthetic product has very largely replaced the natural emery. The raw material is bauxite, a hydrous oxide of aluminum, first calcined to remove all water. It contains various impurities such as silica, oxide of iron, oxide of titanium, etc. The calcined bauxite is mixed with sufficient carbon to insure the reduction to the metallic state of the several impurities, but insufficient to take care of the alumina, and iron is added to make a low grade ferro silicon. This mixture is fused in an electric furnace, the heavier reduced metals tending to sink to the bottom and the lighter fused alumina to float on top of the resulting melt. One of the most important features in the production of such an abrasive material is control of grain size. The furnaces, therefore, are rarely tapped but the mass is allowed to cool, under carefully controlled conditions, in the hearth of the furnace itself. When the hearth is filled with product and has cooled to the proper degree the furnace itself is dismantled and the block pulled out, broken up, and sorted. The abrasive is sent to the crushing plants and broken down to commercial sizes from which are produced the grinding wheels, paper, etc. The actual production of the grinding wheel is largely a development of the ceramic art, the individual grains of abrasive being bonded into the wheel by binders of the porcelain or clay type and burned in suitable furnaces.

Besides influencing grain structure, the introduction of small amounts of various foreign oxides can impart various properties to these abrasive materials,

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[7] For details of the uses of acetylene see Chapters 8 and 31.

hence there is careful choice of the bauxite and carbonaceous materials charged into the fusion furnace.

Silicon Carbide—When silica is heated to a very high temperature in contact with an excess of carbon, a carbide, SiC, is formed. This is the basis of the well-known abrasive called "Carborundum."[8] The reaction by which it is made may be represented:

$$SiO_2 + 3C = SiC + 2CO$$

The arc furnace used in the production of calcium carbide or fused alumina cannot be employed in the manufacture of silicon carbide, because of the possibility of overheating. Although a high temperature is needed for its formation, if that temperature is exceeded metallic silicon will be volatilized from the formed silicon carbide, and graphite will be left behind. It was this accidental discovery that led to the development of the artificial graphite industry to be described later.

FIG. 2. Silicon Carbide Furnace. (Courtesy Carborundum Co.)

In practice the silicon carbide furnace consists of a bed of firebrick 40 ft. long and 6 ft. wide serving as a permanent foundation. The side walls are laid dry and torn down, and replaced with each run of the furnace. The mixture with which the furnace is charged, 3.5 parts of carbon, 6 parts of sand and 1.5 parts of salt, is next shoveled on this foundation, carrying up with it the side walls as necessary for its retention. Through the center of this mixture is placed a core of granulated carbon which serves as the resistor in the furnace. The ends of this core are in contact with permanent end connections, consisting of carbon bars between which the copper conductors are laid. Such a furnace takes about 2,000 H.P. and runs for 36 hours, at the end of which time 6 to 8 tons of commercial silicon carbide have been made.

After such a run the granulated coke forming the heating core has been graphitized, and immediately surrounding and in contact with it is a layer of graphite produced from overheating the silicon carbide first formed there. Sur-

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[8] Reg. Trade Mark.

rounding this graphite is the crystallized silicon carbide in a layer a foot or more thick, beyond which is found the reduced and uncrystallized carbide, the partially reduced mixture and finally unaltered mixture. The last three products are usually charged back into the next furnace run, though an attempt has been made to utilize the partially reduced material as a refractory.

Borides—Of very recent development are new abrasives of which boron carbide is a typical representative. This is an electric furnace product in which a boron oxide is reduced by carbon usually in the presence of a fluxing element or matrix. The crystals formed by solidification in the matrix, are then separated by mechanical means. There are a number of these extremely hard carbides and borides and combinations that are now being produced commercially. They are even harder than silicon carbide but still far from the hardness of the diamond as measured by any lineal absolute scale.

MISCELLANEOUS PRODUCTS

Artificial Graphite—The overheating of a silicon carbide furnace led to the discovery that by suitable decomposition of a carbide, graphite is left behind. Heating of pure carbon will not transform it into graphite, as it must first to pass through a state of a carbide, which requires that some metal or metallic oxide be mixed with it. In practice, anthracite carrying 8 to 10 per cent ash, uniformly distributed through it, is used for the furnace charge. The ash furnishes the necessary metallic oxides. It may be either molded into shape first and then graphitized, or else graphitized in powdered form and then used for all purposes of ordinary graphite. It is practically pure, running over 99.5 per cent graphite, all the other impurities having been volatilized at the temperature of the furnace. In the graphitizing of small electrodes they are packed transversely into a furnace which bears some resemblance to the silicon carbide furnace. Between the piles of electrodes thin layers of granular carbon are inserted and the whole furnace covered over with silicon carbide residue. The current is led in through the massive electrodes at the end and traverses both the pile of electrodes and the granular packing. The major portion of the heat is generated in the granular portion of the circuit. Such a furnace is 25 ft. long and consumes about 1,000 H.P., the run being about 20 hours.

Both the silicon carbide furnace and the graphite furnace were the invention of E. G. Acheson.

Carbon Bisulfide—Much of the carbon bisulfide produced in the world is made in the electric furnace. Whether produced in the old type retorts or in the electrothermic way the raw materials are the same: sulfur and charcoal. The reaction is a relatively low temperature one and the use of electricity is based upon convenience as well as long life of equipment rather than upon any particular inherent properties of the electric current.

In general the electric furnaces are tall cylindrical structures of refractory material divided by an inner cylinder into a central shaft and an annular space. The inside shaft is filled with charcoal and provision is made for feeding sulfur into the annular space. Carbon electrodes project through the walls to contact the charcoal. On passage of the current, charcoal is heated and as this heat penetrates into the annular space the sulfur melts, and as it comes into contact with the heated charcoal carbon bisulfide is produced. By adjustment of voltage on the electrode system the furnace can be made self-regulating. If it tends to become too hot more sulfur will melt and submerge the electrodes cutting off some proportion of the area of the path of the current, thus increasing the resistance and cutting down on the flow of energy. If the furnace tends to become too cold less sulfur will melt and that portion in the furnace will react, forming the volatile bisulfide and thus increase the area of the path of the current.

This is a very beautiful example of the convenience with which the electric current can be applied to certain types of reaction. The furnace itself is built of refractories that do not deteriorate under the existing conditions and since the heat is internally generated there is no wear and tear of retort due to external firing. The efficiency of such a furnace is very high.

Carbon bisulfide finds its greatest use in the manufacture of rayon by the viscose process. Alkali cellulose is combined with carbon bisulfide to produce viscose which is further treated to produce almost 80 per cent of the American rayon production.[9] Carbon bisulfide is also of value as a solvent, as a raw material in the manufacture of carbon tetrachloride, in the vulcanization of rubber, and to some extent in the paper industry. Over 155,000,000 pounds of carbon bisulfide are produced annually and sold for some $5,000,000.

Phosphorus—At the present time the electrothermic production of phosphorus is one of the most rapid growing of the electrochemical industries. It is true that yellow phosphorus has been produced in the electric furnace for the past fifty years but because of the high cost of the relatively small units used for the greater part of this time, it found its outlet only in the match industry and in a few of the more expensive phosphorus compounds. Of recent years the development of the phosphorus producing unit has been such as to produce this element on a large scale and at such low cost that it can be oxidized to phosphoric acid in competition with the older wet methods of production.

Readman Process. This was the original of the electric furnace phosphorus processes and the principles upon which it operated are essentially the same as those existing today in the modern high powered furnace.

Tricalcium phosphate in the form of phosphate rock or bone ash is fused with some form of carbon and silica in a closed electric furnace, the reaction being

$$Ca_3P_2O_8 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + P_2 + 5CO$$

The phosphorus vapor and carbon monoxide gases are conducted from the top of the furnace through a condenser which delivers liquid phosphorus. The yield of phosphorus is estimated to be about 2 pounds per electrical horsepower day (18 K.W.H.)

The Readman furnaces were very small running only a few hundred H.P. Nearly twenty years ago attempts were made to use much larger furnaces of the multi-phase type for the production of ferrophosphorus. In these furnaces scrap iron, phosphate rock, carbon and a flux were smelted together producing a ferrophosphorus running about 20 per cent in phosphorus. The slags made were silicates of lime. It was found that not all of the phosphorus could be

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[9] See Chapter 38.

reduced into the ferroalloy if the grade was to be above 20 per cent, and that the slags carried material quantities of phosphoric acid as silico-phosphates, unless an excess of carbon was added to the charge. Under this latter condition the slags could be freed of phosphorus but a considerable proportion was evolved in the elemental state in the form of vapor. By putting a closed top on the furnace and admitting air under the roof these vapors oxidize to phosphoric oxide and this could be recovered from the gases by suitable scrubbing or electrostatic precipitation. The product is a high grade concentrated phosphoric acid since even with electrostatic precipitation it has been found advantageous to introduce steam into the gas current.

More recently developments tended toward feeding a mixture of phosphate rock, clay and silica to a closed type multi-phase furnace. Sufficient coke is added to the charge to reduce the phosphates to elemental phosphorus. This is taken from the closed furnace to condensers and cooled until liquid. In other words this modern development is simply the old Readman process carried out on a greatly enlarged scale.

The liquid phosphorus is run into storage tanks provided with heating coils and is handled through pumps and pipe lines much like any other liquid. It is even being shipped in tank cars to various consuming centers. It is a comparatively simple matter to burn the phosphorus in air to phosphoric acid which is recovered through scrubbing as strong acid and of very high purity. Some half dozen installations are in operation in this country and several in Europe. Most of the furnaces are three-phase closed type with continuous electrodes. Because of the low content of coke in the charge the voltage is relatively higher than in most electric furnace operations.

Sodium and Potassium—Although sodium and potassium are metals, their uses are largely confined to the straight chemical field, so their production is discussed here, rather than in the chapter on non-ferrous metals.

Production from Caustic. Sodium is produced on a very large scale. The first successful electrochemical process and one still operated in a number of plants consists in electrolyzing a fused bath of caustic soda. The caustic is dehydrated as far as possible by thermal methods and the last traces of water are removed by preliminary electrolytic treatment. When the last of the water has been eliminated, metallic sodium appears at the cathode along with an equivalent amount of hydrogen, and oxygen at the anode. The fusion pots are of iron and both anode and cathode of either iron or nickel. A metallic screen serves as a partial diaphragm for retaining the molten sodium near the cathode so that it can be ladled out of the cell from time to time.

The operation requires very close control for the sodium has a tendency to dissolve in the bath of molten caustic and diffuse to the anode, this tendency increasing sharply with rising temperature. In practice, therefore, if high current efficiency is to be attained it is necessary to operate just as closely as possible to the melting point. Since both hydrogen and sodium appear in equivalent quantities at the cathode the current efficiency computed on the sodium alone can never exceed 50 per cent. At a temperature of only 20° above the melting point of the caustic the actual efficiency will have dropped down as low as 40 per cent, indicating the precise control necessary to obtain the maximum effectiveness of the current. Approximately 3 H.P. years are required per ton of sodium starting with caustic soda.

Production from Salt. Because of the low current efficiency of the caustic process, attempts were made over a long series of years to produce sodium by the direct electrolysis of molten salt. The many difficulties have been overcome and probably the larger bulk of the world's production of sodium is now made by this process. The cell which is used consists of a rectangular box of structural steel lined with refractory material. It is closed at the top, for one of the products of decomposition is chlorine which must be collected. The cathode is made of iron and the anode of graphite and a wire mesh diaphragm surrounds the cathode to retain the sodium which floats on top of the molten bath of the chloride and is removed by a siphon arrangement. Chlorine is collected from the anode compartment, cooled and placed on the market in the usual forms.

The bath material itself consists essentially of molten salt to which various additions of other salts are made to reduce the melting point as far as possible. However, these concentrations of foreign salts must be limited to relatively small quantities otherwise the sodium will be contaminated. These agents are various fluorides and chlorides of the alkali and alkaline earth metals, such as $CaCl_2$. Such a bath, when molten, has a relatively high conductivity and the resistance offered to the passage of the electrolyzing current is not always sufficient to maintain the heat losses of the sodium. Provision, therefore, must be made to supplement the energy supplied to this cell by superposing sufficient alternating current to make up for this heat deficiency.

Difficulty is experienced with contamination, principally from the refractory lining, and of secondary importance, from the electrodes and the diaphragm. Therefore, it is necessary from time to time to discard these fused baths and replace with fresh material. The life of the bath is relatively short on the average and provision, therefore, must be made for tapping these furnaces and supplying fresh molten bath to them.

The energy requirements for this process may be figured at approximately 2.5 H.P. years per ton of metallic sodium. Chlorine, however, is a credit in this operation. Current efficiencies are relatively high; of the order of 80 to 90 per cent in an operating cell in good condition, for we do not have the same limitation of having to separate hydrogen along with the sodium in this case of direct electrolysis of molten salt.

Production of Potassium—For the production of potassium the electrolysis of caustic potash, and similar to that for sodium when using the same cells, is universally used. The quantity of potassium produced, however, is relatively small as compared with the great tonnage of sodium which finds an enormous outlet as sodamide in the cyanide and dyestuff industries, and for the production of the sodium-lead alloy used in producing tetraethyl lead.

THE STORAGE BATTERY

The manufacture of lead storage batteries is now one of the large industries of the country. The enormously increased demand for starting batteries, by the automobile industry, added to the use of batteries for motive power of many types of self-moving vehicles, has called for ever-increasing production.

The overall equation of the reactions taking place in the lead storage battery may be written as follows:

$$\mathrm{PbO_2 + Pb + H_2SO_4} \underset{\text{discharge}\longrightarrow}{\overset{\longleftarrow\text{charge}}{\rightleftarrows}} \mathrm{2PbSO_4 + 2H_2O}$$

The left-hand side of this equation represents the charged plates and the right-hand side the discharged plates. Hence, the charged lead cell consists, essentially, of a plate of lead, a second plate of lead peroxide, held apart by a porous "separator" through which sulfate ions can migrate—all immersed in a sulfuric acid solution. The problem of producing a storage battery of high capacity and efficiency is largely one of incorporating the correct physical and chemical properties to the plates of lead and lead peroxide.

The original lead storage battery was made by suspending two plates of soft sheet lead in a bath of dilute sulfuric acid of specific gravity of about 1.2. One plate was connected to the positive terminal of a source of direct current and the other plate to the negative source. Current was supplied for a short interval of time and then cut off and the two plates short-circuited. This operation was repeated a large number of times until the plates were "formed." At first these plates had little capacity for storing up potential chemical energy which was afterwards transformed, on discharging, into electrical energy, but as the operations of charging and discharging were repeated the capacity of the two plates increased materially. Such batteries, however, would have been of no value for the present-day service in automobile starting, for the stored capacity per unit of weight was small and the apparatus itself was incapable of taking the abnormal starting loads of the modern automobile.

The modern battery plate consists of a grill of cast antimonial lead carrying from 5 to 10 per cent of antimony. The grids vary from 2 to 5 mm. in thickness. Into this grid is pressed a paste consisting of lead oxide mixed with sulfuric acid or ammonium sulfate. This paste is packed tightly into the mesh of the grids and left to harden. The plates are then suspended in open tanks, those intended to be anodes connected to a positive source of current and those which are to be cathodes to a negative pole. Under careful regulation of the current these pasted plates are "formed," that is, become active by transformation of the oxide paste of the anodes to lead peroxide and the oxide paste of the cathodes to spongy lead. Great care is needed in the forming of a plate to gain the maximum adherence of the paste without warping the supporting structure.

After formation the plates are washed, dried and stored for assembly. Depending upon the size and rating of the battery a certain number of anode plates are burned to a lead strap; for a 13-plate cell 6 anode plates are grouped together. Similarly the cathode or negative plates are burned to a strap, there being one more negative plate in a battery than positive plate. For assembling the battery, the anode and cathode groups are meshed together with insulating separators between the plates. These separators take various forms, such as thin strips of wood veneer, thin perforated pieces of hard rubber, or various patented compositions. When put into service, the battery is filled with a high purity dilute sulfuric acid of strength between specific gravity 1.2 and specific gravity 1.3.

The ordinary starting battery contains either 13 or 15 plates per cell with three cells in series. The 13-plate battery has a capacity of storing up energy equivalent to 100 ampere hours and the three cells in series will deliver current at 6 volts potential, that is, approximately two volts per cell.

The usual storage battery, when new, will deliver from 80 to 90 per cent of the energy used in charging, but as the battery becomes older this efficiency drops off rather sharply. As the battery ages the anodes buckle and shed their paste and the cathodes become clogged with sulfate and lose their porosity. This prevents a diffusion of the sulfuric acid into the plates and hinders charging.

The Edison Cell—Another type of storage battery, the so-called "iron nickel" or Edison cell, uses a spongy iron anode and a compressed flake nickel cathode, in a solution of 15 per cent caustic soda containing a small amount of lithium hydrate. The chemical reaction involved in this cell is:

$$Fe + 3H_2O + Ni_2O_3 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Fe(OH)_2 + 2Ni(OH)_2$$

This battery cannot be used for starting purposes but has given excellent service for motor operation and ignition. It delivers a moderate current but is incapable of furnishing the peak surges for starting a motor. It has the great advantage of not being injured by complete discharge, which is not true of the lead battery.

Dry Cells—The old wet primary batteries have largely disappeared and their place has been taken by the "dry cell." This cell is not exactly dry as the name implies, but it at least contains no free liquid. These cells are manufactured by the millions and of all shapes and sizes to meet the wide variety of demands in the radio, flashlight, ignition and signal systems. The positive pole consists of a carbon rod. Surrounding this rod is a mixture of manganese dioxide, finely powdered graphite, and ammonium chloride made into a paste. The whole is packed in a cylindrical container made of sheet zinc which also serves as the negative pole. A cardboard or paper carton surrounds the zinc casing, serving both as a protective coating and an insulating medium. The contents of the cell are sealed in by molten pitch or sealing wax cast into place. Formulation of the active mass varies not alone among the different manufacturers, but is also dependent upon the size of the cell and its intended use. Great care must be taken in the purity, size of grain and mixing of the ingredients to insure a long shelf life and quick recuperation in service. A well-constructed dry cell should show 1½ volts electromotive force and should be capable of shelf storage on open circuit over several months without deterioration.

Electroplating—A branch of electrochemistry that has attained enormous commercial importance, is that of coating the surface of one metal with a thin skin of another either for decorative or preservative purposes. Thus base metal is coated with gold for decorative purposes, iron with nickel for preservative reasons. Practically all of this metal coating is now done by suspending the object to be plated as cathode in a suitable bath and electrolytically depositing a coating of the desired metal on its surface. It is not possible here to cover thoroughly all the methods and solutions used in this work, as each establishment seems to cherish its own secret manipulation, a great deal of which secrecy is more imagined than real.

To insure uniform results the base metal to be plated should be sound, free from pores and sand holes, and above all, clean. Cleaning is done by the use of brushes, buffing wheels, acid and alkali baths; the objects to be plated not being touched by greasy hands.

The composition of the baths used are as varied as the establishments, each seemingly possessing its own special formula for each bath. Chemically, the baths are, as far as possible, so constituted that metal is not deposited by simple chemical replacement, as such coatings are usually not strongly adherent. A general idea of the baths used may be gained from the following:

Copper. The solution contains 10-12 per cent copper sulfate and 2-3 per cent sulfuric acid. For plating on iron, this solution, because of chemical replacement, does not give a particularly good adhering coat and recourse is had to first plating a very thin coating of copper on the iron from a copper cyanide solution, the object finally being finished in the acid bath, for the reason that regeneration of the cyanide bath by the use of a copper anode is not particularly successful. Such a cyanide bath may be prepared by dissolving a mixture of one part of copper carbonate and three parts of potassium cyanide in twenty-five parts of water.

Silver. A fairly strong solution of the double cyanide of silver and potassium or sodium is most frequently used in plating this metal.

Gold. A similar solution of the double cyanide of gold and potassium is used.

Zinc. Formerly, most of the galvanizing or zinc coating of iron was by the so-called hot method; that is, carefully cleaned sheets or objects of iron were dipped in a bath of molten zinc. The surplus adhering to the surface was then wiped off and there resulted the typical bespangled appearance of galvanized sheet. To the uninformed this crystalline appearance denoted a high quality coating. In more recent times it is recognized that an electroplate of zinc of equal or better quality could be produced and more and more of the zinc coating is now produced by the electrochemical method.

For complicated batches, as for example screw threads, the electrochemical method permits the formation of a uniform coating preserving all of the characteristics and dimensions and without possibility of warping. Further, it is now possible to operate the electro-galvanizing process mechanically. Small articles are plated in tumbling barrels. Conduit and tubing can be handled on mechanical carriers through the bath. Wire, strip and sheet stock are run continuously through the cleaning, washing, plating and final washing baths.

One of the most interesting examples is the continuous electro-galvanizing of wire, the whole operation being mechanical and taking place in a series of tanks through which the wire is fed. An excellent finish can be given by finally running the galvanized wire through a series of dies which give it a hard, polished surface. It is even possible in these highly developed continuous plating operations to use roasted zinc concentrates for maintaining the strength of the bath, and insoluble anodes, so that we have here not only the metallurgical recovery of the zinc from its ore but its direct placement on a finished article.

Nickel. A saturated solution of the double sulfate of nickel and ammonia is largely used for nickel-plating. As nickel anodes do not dissolve in sufficient quantity to recuperate this bath, nickel sulfate is added from time to time to maintain its saturated state.

Chromium. The very valuable properties of chromium; its extreme hardness, its resistance to oxidation and its resistance to scaling, as well as its bright and pleasing appearance, have created a tremendous demand for chromium-plated objects. The plating bath consists of a mixture of chromic acid and chromic sulfate. Various forms of insoluble anodes have been successfully operated. Most baths work with lead anodes. For bright plating, it is customary first to nickel-plate and buff before plating with chromium.

Cadmium. Because it gives an excellent protective coating combined with a steel-gray color and is capable of taking a high polish, cadmium plating has found considerable application on hardware, instrument cases, and aeroplane parts. It is plated from cyanide solutions, made by dissolving cadmium salts in sodium cyanide. The anodes are cadmium.

Brass. A mixture of cyanides of copper and zinc containing varying proportions of the two metals, depending on the color of the plating desired, will yield a plating of brass. Great skill is needed to use such a bath and much secrecy is maintained regarding the exact composition of a successful brass bath.

Rubber. While properly not a true electroplating operation, nevertheless rubber has been deposited by the use of the electric current. The underlying phenomenon of depositing by use of the electric current is very complex. The latex is suspended in an extremely dilute, slightly alkaline medium which is placed in the cell. As anode, zinc has been found to be the most successful. High voltage is then applied to the cell, creating a strong electrical field between the two electrodes. The suspended particles of latex, which are negatively charged, move toward the anode and there attach themselves. Various solids, such as sulfur, fillers, pigments, and even super-accelerators can be suspended in the solution along with the latex and be deposited with it. By this process rubber can be formed or molded in its final shape and be readily vulcanized. The deposited rubber has an extremely high tensile strength and elongation, and is in general superior to milled rubber.

After withdrawal from the bath the plated object is thoroughly washed with water, or even alkali if an acid bath has been used. Dull or matte finishes are given to a plated object by the use of a wire or scratch brush. Polishing is done with rouge, whiting or other polishing powder on a cloth or leather wheel. In many cases this mechanical manipulation after plating plays a more important part in obtaining a desirable ornamental finish than the actual plating operation itself.

PIGMENTS

The electrolytic manufacture of pigments has attracted a great deal of attention, but up to the present time has attained no great prominence because of the many unsolved technical difficulties. The production of white lead[10] by the electrolytic dissolution of a lead anode and subsequent precipitation of the basic carbonate is in commercial use, in a small way. The electrolyte used consists of a dilute solution of sodium carbonate to which is added a much larger portion of a sodium salt whose acid radical forms a soluble compound with the lead.

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[10] For a discussion of the chemical methods of producing white lead, see Chapter 26.

Chlorate or nitrate is used for this purpose, it having been found that the use of such a salt in the bath prevents the lead carbonate formed from adhering to the anode and thus insulating it. The caustic formed at the cathode of the cell is immediately neutralized by the introduction of a current of carbon dioxide, thus directly supplying the ingredients used in the process in the form of sheet lead anode and gaseous carbon dioxide. The greatest difficulty met with in commercial operation is the dropping of small pieces of undissolved anode into the deposit of white lead at the bottom of the cell, which causes poor color. Another difficulty is the tendency to form crystalline precipitate, a most undesirable product.

Lead chromate can also be obtained in the same manner by using a bath of potassium dichromate and nitrate, regenerating the solution with chromic acid. The sulfides of cadmium, antimony, etc., have also been made by the use of these metals as anode in a solution of sodium hyposulfite, though the process has never attained much commercial prominence.

OXIDATION AND REDUCTION OF ORGANIC COMPOUNDS

A broad general view of electrolysis would consider an anode dipped into an electrolyte as a reducing agent; each 96,540 coulombs of electricity passing through it causing the production of one gram-equivalent of a substance of unit valence. A cathode is similarly a reducing agent, the passage of the above quantity of electricity causing a reduction of one gram-equivalent of unit valence. We have here an ideal means of reduction, in that no foreign materials, not essential to the reaction, need be added to cause the desired change, and there is hence no contamination of the resulting products to fear. Electrochemical reductions resolve themselves into a choice of suitable electrode materials, current densities and separation of the effects of anode and cathode through diaphragms. In the field of organic chemistry many applications have been made of electricity to the reactions of reduction, where conditions are suitable to their use, but strange to say not many are today on a commercial scale. A few of the prominent commercial processes are the following:

Chloroform—A solution of 20 per cent sodium chloride, to which acetone is added, evolves chloroform on the passage of an electric current. The chloroform vapors are removed from the closed cell and condensed. The direct use of chlorine produced in the caustic soda industry for this purpose is of much greater technical importance than the above direct process.

Iodoform—A solution of potassium iodide to which alcohol or acetone is added, and the whole electrolyzed, yields a solution of iodoform, which can be crystallized out by cooling. This process is the basis of an important manufacturing industry at this time, and has largely supplanted the old chemical process.

Sorbitol and Mannitol—Probably the most important of the organic processes based upon the chemical action of the electric current, is the reduction of the sugars to the corresponding alcohols. For example, the electrolytic reduction of glucose, that is, the reduction of the aldehyde group in glucose to the corresponding hydroxy group (CHO to CH_2OH), is now carried out on a large scale.[11]

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[11] Taylor, R. L., Chem. & Met. Eng., *44*, 588 (1937).

In similar manner mannose is reduced to mannitol. The corresponding sugars are dissolved in a solution carrying free alkali and treated in the cathode compartment of an electrolytic cell. Here the sugars are reduced to the corresponding alcohols which are recovered from the cathode liquor. This is probably the largest commercial example of direct organic synthesis at the present time.

In recent years electrolytic oxidations and reductions of organic compounds have attracted a great deal of attention in the laboratory and thousands of patents covering this field have been applied for. In only a few cases has the electrolytic process been able to compete with the older existing purely chemical treatment, but it is anticipated that there will be a very marked advancement in this art in the next few years. The problems of proper solvents, of diaphragms, of control are slowly being solved in the laboratory and pilot plant and we may expect very greatly increased development in this most interesting field.

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CHAPTER 13

FERTILIZERS

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The growth of plant life is necessary for its own perpetuation and in addition is a tremendous factor in the preservation and well being of man. By far the greatest part of man's food comes either directly from plant life in the form of vegetables, fruits, grains, and the like, or indirectly as meat from animals fed and fattened on products of the soil.

The growth of plant life requires sufficient sunshine, water and carbon dioxide, and certain compounds of elements, among which the prime requisites are nitrogen, phosphorus, and potassium compounds. All green leaves, when in healthy condition, at suitable temperatures and with sufficient illumination, can produce carbohydrates (starch or sugars) from carbon dioxide and water by the processes [illegible] photosynthesis. Photosynthesis is performed by the chloroplasts and goes on [illegible]perfectly or not at all in all plants in which no chlorophyll exists.

For the most part nature has done her part quite well in supplying adequate [illegible]ine, water in the air and soil, and carbon dioxide in the atmosphere. How[illegible]he remaining limiting factor, the required mineral compounds, are drained [illegible] soil by the repeated growth of plants. If these compounds are not [illegible] into the soil the result is a depletion of the soil and, sooner or later, s[illegible] plant growth is impossible. It is this phase of plant nutrition with wh[illegible]ust concern himself, and which has become first the art and finally the [illegible] fertilization.

FERTILIZER MATERIALS AND THEIR COMPOSITION

[illegible]torical—As far back as records go, the value of animal manures has been [illegible]ed in the growing of crops. Why they were of benefit and what relation [illegible]stituents bear to those of plants are matters that have only been worked [illegible] the past century. The earliest record of the use of mineral fertilizers is [illegible]ed in a paper by Sir Kenelm Digby printed in England in 1669. In [illegible]per the use of saltpeter as a stimulant to plant growth is advocated. In [illegible]eo. de Saussure pointed out the significance of the ash of plants, and [illegible]that without it plant life was impossible. Justus von Liebig in 1840 and [illegible] really the first to lay down the foundation of present fertilizer pract[illegible]the middle of the nineteenth century the importance and value of nitrog[illegible]horic acid and potash was pretty well known and it is from this time th[illegible]eal growth, both of the use and knowledge of commercial fertilizers, d[illegible]

Mineral nitrogen as a fertilizer was first obtained from saltpeter, and phosphoric acid from bones. Later, nitrogen compounds were obtained from by-products of slaughter houses (organic nitrogen) and from ammonium sulfate, a by-product of coke-ovens,[1] and as synthetic cyanamid and ammonia made from the nitrogen of the air.[2] Phosphoric acid was obtained from both petrified and fresh bones and from mineral phosphate beds in various parts of the world. Until the World War of 1914-1918, the main source of potash was from the mines of Stassfurt, Germany. Since then numerous other deposits have been discovered and plants put in operation so that the world is no longer dependent on Germany for this material.[3]

Essential Elements for Plant Growth—Broadly speaking, there are three classes of fertilizer materials: those which in themselves are a direct source of plant food, those which by their action, tend to make plant food materials more available, and finally a number of metallic elements whose action is not definitely known but still are absolutely essential to the proper development of plant growth. The essential nature of these certain elements essential to plant growth has caused considerable work and speculation as to their exact action and determination.

The Most Essential Elements—The elements which are most essential for plant food are nitrogen, phosphorus, and potassium. To be available to plants, they must be present in the soil in some chemical combination which is water soluble, at least to a limited extent.

Fertilizer dealers and experiment-station bulletins treat the different forms of fertilizer materials separately, and a familiar understanding of these trade names is important.

Ammonia is expressed either as nitrogen, as ammonia, or as nitrogen "eq[illegible] lent to ammonia." There are various conditions in which phosphoric aci[illegible] be expressed, such as reverted, available, insoluble, total, and phosph[illegible] "equivalent to bone phosphate of lime."[4] Potash is expressed as pot[illegible] as potash actual, or as potash equivalent to sulfate of potassium or [illegible]e of potassium.

All genuine commercial fertilizers owe their value to the kind[illegible] and amount of nitrogen, phosphoric acid, and potash they contain. [illegible] made by mixing more or less of the several kinds of raw materials fur[illegible] t[illegible] sired ingredients, and to these may be added sulfuric acid to render the pho[illegible] acid available and a filler to make up the desired formula.

Nitrogen (*Ammonia*). The nitrogen in fertilizers is always combi[illegible] other elements and may be present in one or more different forms, such a[illegible] nitrate, ammonium sulfate, or in the form of organic nitrogen as found [illegible]l matter, such as blood, tankage, guano, or in vegetable matter, such as [illegible]d meal.

Nitrogen is expressed as total nitrogen, mineral nitrogen, orga[illegible]gen, water-soluble and water-insoluble mineral and organic nitrogen. [illegible]s of nitrogen for which value is given must be in the "available" fo[illegible] such

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[1] See Chapter 15.
[2] See Chapter 8.
[3] See Chapter 9.
[4] Phosphoric acid as used by the trade is not H_3PO_4, but the pen[illegible]$_2O_5$).

condition that it may be available to the growing plant as a food. The availability is determined by standard methods of analysis.

Phosphoric Acid. This as used in fertilizers does not exist as true phosphoric acid, but as various salts of phosphoric acid and lime. Soluble phosphoric acid is the monocalcium phosphate formed during the process of acidulating phosphate rock or bone. Reverted phosphoric acid is the dicalcium phosphate which is also formed during the process of acidulation and is soluble in neutral ammonium citrate. Available phosphoric acid is the sum of the soluble and reverted forms and is the total phosphoric acid in a condition capable of being absorbed by plants.

Insoluble phosphoric acid is the tricalcium phosphate as it exists in phosphate rock and bone and is not available for plant food. Total phosphoric acid is the total amount present irrespective of the form in which it is present. It is the sum of the above three forms. Phosphoric acid equivalent to bone phosphate simply means the total phosphoric acid calculated as the tricalcium phosphate.

Potash. This term as applied to fertilizers always means the oxide of potassium. It is not found as such in fertilizers, but as either chloride, sulfate, nitrate or carbonate of potassium, or as organic potash.

Potash soluble means the actual K_2O soluble in water and is the only kind considered in fertilizers.

Expression of Formulæ. One often sees formulæ expressed in this manner, 4-8-2, or 3-6-4. It means that nitrogen comes first, phosphoric acid next, and potash third, hence the 4-8-2 indicates a fertilizer containing 4 per cent of nitrogen, 8 per cent of P_2O_5, and 2 per cent of K_2O.

The Trace Elements—It has been found that, in addition to the three principal elements, nitrogen, phosphorus and potassium, plants require small amounts of the "trace" elements which occur to a limited extent in nearly all soils.

Winifred E. Brenchley [5] has published a paper which presents a valuable compilation of data with reference to "work done on the possible essential nature of certain elements for plant growth during the last five years."

"Until about the beginning of this century, ten or eleven elements only were generally considered as essential for normal growth of plants. The presence of other elements in minute quantities was recognized in many plants, but their possible association with nutrition and growth was not understood. The activities of the French investigators from 1897 onwards focussed attention on the function of these minimal traces of elements, and the work of Bertrand on manganese, Javillier on zinc and Agulhon on boron may be regarded as the foundation of the widespread investigations which are now of such practical economic importance.

"The French school claimed that some of these minor elements were essential for the full development of certain plants but the experimental difficulties in obtaining adequate proof were not at that time fully overcome, and for a time the matter remained of academic, rather than practical, importance. Still, interest had been awakened, and much experimental work resulted in many and varied claims being made for different elements—claims which frequently were not borne out by other tests under different conditions. In 1923, however, Warington was able to prove conclusively that a trace of boron is absolutely essential

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[5] "The Essential Nature of Certain Elements for Plant Nutrition," The Botanical Review (April, 1936).

for the development of *Vicia faba*, as in its absence the meristematic tissues die and growth is impossible. Since then, investigations all over the world indicate that boron is probably essential for all plants in varying degree and that certain obscure plant diseases may be due to a deficiency of this element.

"Although it is more difficult to get clear-cut proof of the essential nature of manganese for all plants, the whole body of evidence is now so strong that this statement is generally accepted as fact. The small amount that is necessary and the closeness of the association of manganese with iron render this element peculiarly difficult for experimental treatment. Copper and zinc have also attracted much attention and their value in certain cases seems evident, though they cannot lay claim to the importance of manganese and boron."

To illustrate the action of a few of these vital elements it is necessary only to examine a few results obtained by their use.

Manganese—50 pounds to the acre greatly increases yield of tomatoes and other crops, such as spinach, corn and soybean.

Boron—10 pounds borax to the acre on celery soils of Florida prevents cracked stem and tremendously increases yield; 20 pounds will damage the crop.

Zinc Sulfate—15 to 20 pounds per acre controlled white bud and increased corn crop. Also improves cowpeas, peanuts, oats, Napier grass, sugar cane and crotalaria. Also controls pecan rosette when used in iron sprays.

Copper Sulfate—50 pounds per acre increases yield of beans. Corrects die-back and ammoniation in citrus belt.

Other elements either known to or suspected of having an influence on plant growth are magnesium, lead, tin, and a number of others.

Experimental work is being carried on very extensively along this line.

When natural materials are used for making fertilizers these necessary "trace" elements are supplied to greater or less degree. For instance, Chilean nitrate contains (shown either by chemical or spectographic means) aluminum, barium, beryllium, bismuth, boron, calcium, caesium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, nitrogen, iodine, potassium, silicon, silver, lithium, molybdenum.

In general it may be said that all natural raw materials used in the manufacture of fertilizers contain at least some of these minor or vital elements; such materials as phosphate rock, potassium salts, meals, tankage, blood, etc.

Sulfur Requirements of Soils. The average amount of sulfur in soil 3 feet deep is 5085 pounds per acre; this amount would be used up in from 70 to 285 cropping seasons, figuring on minimum and maximum requirements of various crops. In neighborhood of cities the sulfur is replenished from the air, but not in country districts. Thanks to the old plant ash analyses, investigators were misled until quite recently on the sulfur content of plants. The conception based on old analyses was that plants used so little sulfur that the average soil contained a sufficient quantity of this element to answer the requirements of plants almost indefinitely. Ideas on sulfur underwent rapid evolution, however, when it was shown that only an insignificant part of the total sulfur is retained in the ash. This is due to the fact that a considerable proportion of the sulfur is present in organic combination. A definite benefit is derived by adding sulfur compounds to some soils.

FACTORS AFFECTING AVAILABILITY

Japanese Fertilizer—Soil fertilization is not necessarily merely a matter of supplying a certain number of compounds in given proportions. Physical structure of the soil is a very important item. The so-called "Japanese Fertilizer" is an example of a material which may function both as a source of fertilizing elements and a soil conditioner. This fertilizer is a product called "promoloid," a colloidal silicate of magnesium. The makers state that "it is not a manure, but an agent which accelerates the growth of vegetables, improves their taste, color and form, and enables an unusually fine crop to be realized."

The following explanation of the origin of the material is given by the manufacturer. Some districts in Japan are noted for the early production of vegetables of the best quality, such yields being limited to certain tracts of land. The crop in neighboring soil, under similar conditions of planting and cultivation, is distinctly inferior. These limited areas of specially productive soil are found in widely separated parts of the islands. A careful analysis of the soil from each of these districts disclosed the fact that colloidal magnesium silicate was common to all of them. It seemed likely that this element contributed to the exceptional yields from these soils.

Function of Soil Moisture in Fertilization—Evaporation of soil moisture cools the soil, as the heat necessary to vaporize the water is drawn from the land. Evaporation, however, draws the moisture from below for very considerable depths and the fertilizing matters suspended or in solution are brought by this process within reach of the roots. To quote from some Wisconsin experiments: "Soil water is constantly in motion. When rain falls the moisture sinks into the soil, carrying along with it oxygen, carbonic acid, nitric acid, ammonia, etc., and rendering plant food available, a part of which may be lost in the drainage if the rainfall is excessive. When the rainfall ceases, evaporation commences and the soil water begins to rise, carrying along with it dissolved plant food which accumulates in the surface soil. This power which soils have of drawing up water from their lower depths is known as capillary attraction and may extend down 6 or 7 feet."

Some idea of the immense amount of soil water thus brought to the surface may be gained from the fact that with the average soil, clay loam under cultivation, 660 pounds of water per square foot is evaporated yearly, that is, 28,750,000 pounds per acre. Computing from the average analysis of soil waters, this quantity of evaporation would bring to the surface soil about 14 pounds of ammonia and 57 pounds of potash; the phosphates do not appreciably enter into water solution.

It must be understood that these fertilizing elements are not gained, they keep constantly in circulation; at night they sink only to rise again when the evaporation commences with the succeeding sunrise. By this circulating system the fertilizing elements are brought within reach of the plant roots and are utilized; were it suspended, the application of manures would have to be increased many fold, as the quantity of the nutrients in the immediate vicinity of the plant itself would have to supply all its requirements; and as the roots of a plant in ordinary farming practice occupy probably less than 5 per cent of the total space, it follows that the efficiency of 1 ton of fertilizer, as at present, would require an application of 20 tons to accomplish the same results with suspended circulation of soil waters. This is why commercial fertilizers contain a disproportionate quantity of phosphoric acid as compared with potash and ammonia; the phosphates, to a great extent, take immediately in the soil an insoluble form and are rendered available as plant food only by the actual contact of the plant root hairs.

Effect of Soil Structure—The previous section indicates that the movement of water in soils is a factor of prime importance in the functioning of fertilizers. This in turn is greatly affected by the physical character of the soil. The general characteristics of a clay soil are fine texture and cohesion of the particles. It absorbs moisture from the air and draws it from the lower soil by capillary attraction, and retains water obstinately. If worked while wet it becomes hard and intractable. A sandy soil has little adhesion of particles, attracts little or no moisture from the air, and allows water to percolate through it readily, thus causing loss of fertilizing elements by leaching. It absorbs and retains heat well and is dry and warm, easily worked and will not bake. Its power of drawing moisture from below is about two-thirds that of clay. Soils intermediate between sand and clay take, in a modified way, the main features of both.

For purposes of agriculture the circulation of moisture in the soil and the temperature are of greatest importance. A soil having clay as its predominant constituent holds its water almost stationary, and when subjected to evaporation, through heat or drying winds, bakes badly. The soil water contains fine particles of clay in suspension and these are drawn to the surface and deposited by the evaporation of the water, thus forming an upper layer no longer porous. Evaporation ceases. The soil moisture, only a few inches below the surface, remains quiescent, and the closely packed upper layer also excludes heat and gases, the soil becomes cold, and those chemical processes, necessary for the preparation of plant food in an assimilable form, cease.

Use of Lime—The best known remedy is an application of lime, which throws down the suspended clay in the form of small granules, thus opening the pores of the soil and enabling a free circulation of water and the admission and action of gases and sunlight. With sandy soils evaporation does not bake and the movement of the soil waters is accelerated, but there is danger of exhausting the supply, as the power of capillary attraction in this case does not greatly exceed a depth of 20 inches. These soils give free play to the action of gases and sunlight and maintain a temperature favorable to vegetation. Excessive evaporation is prevented by thorough tilling; a surface layer of finely pulverized earth a few inches deep arrests evaporation while it still maintains a fair degree of soil porosity and consequently the admission of gases and sunlight is not retarded.

Action of Carbon Dioxide on Soils—Another factor of importance in the functioning of fertilizers is the action of carbon dioxide on the materials in the soil. All fertile soils contain a considerable amount of organic matter, and the presence of oxygen is necessary to accomplish its decomposition. Soils also contain innumerable bacteria, a part of which, at least, are intimately concerned in the decay of organic matter and cannot live without oxygen.

One class of these bacteria decomposes part of the soil's organic matter with the formation of carbon dioxide. Water dissolves its own volume of CO_2 under ordinary pressure, forming a solution of carbonic acid, H_2CO_3. When water is so charged it has a high solvent power for the carbonates of calcium and magnesium, protoxide of iron and manganese. These salts are nearly insoluble in pure water. In this way carbonic acid plays a part of great importance in the growth of plants, since it enables water to convey to plants many fertilizing substances which are otherwise hardly available.

It is interesting to note here that the leaves of plants are white, in the absence of iron, and not green. By means of the microscope, the chlorophyl grains have been seen to grow and continue to prosper, as soon as a little iron was furnished to plants that had previously been without it.

The Variability of Soils—The foregoing brief discussion indicates that soils are complex physical systems and their functioning depends on a number of chemical and physical variables. The study of soils is almost a complete science in itself and is the subject of a great deal of continuous investigation. The problem of what fertilizer treatment is best for a given soil is very complex and is not logically a subject to be discussed in a treatise on industrial chemistry. Hence, the bulk of the rest of this chapter will be confined to a discussion of the methods used in obtaining most essential fertilizer materials.

Loss of Fertilizer Materials—The erosion of American agricultural land has repeatedly been brought to the attention of the public, particularly during the past two decades. Erosion refers to the actual removal of soil from the land. Obviously, this means loss of fertilizer materials. In addition, great quantities of fertilizer material are lost by the leaching of waters which flow over land surface, even if the soil is not removed. The annual loss by erosion and leaching is one of appalling magnitude. It is largely preventable by proper agricultural practice and some progress is being made in its prevention. There are numerous publications which deal with this important item of our national economy. Some of them will be found in the Reading List at the end of the chapter.

NITROGENOUS FERTILIZERS

One of the major revolutions wrought by chemical industry was the development in 1912 of the successful Haber-Bosch process for making synthetic ammonia.[6] While the first use of this synthetic ammonia was that of making explosives it has been progressively used more and more for various industrial products and for fertilizers. Eventually the importance of the use of the limitless quantity of nitrogen in the air for fertilizers will far outweigh the use for explosives or even for the varied industrial uses. But there are very large supplies of natural materials which still supply nitrogenous fertilizers and as long as the deposits last they will probably continue to be a practical source to fit in with at least part of our economic pattern. Hence, it is worth while to review the more important of the natural sources.

Guano—Off the coast of Peru are the small, high, rocky, barren and uninviting Chincha Islands, where rain seldom falls. Yet from them has come vast wealth. Guano to the value of over a billion dollars has been taken from them. It is doubtful if there be another spot of equal size on the earth which has yielded so much wealth as these guano beds. These islands, however, are not the only

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[6] See Chapter 8.

source of Peruvian guano, as the Macabi, Guanape, and Lobos, Ballestas, and the Huanillos, as well as scores of small islands, have also furnished large quantities.

The word guano is the Spanish rendering of the Peruvian word *huanu*, meaning excrement. There are many varieties of Peruvian guano having different fertilizing values due to their different chemical constituents, but they all are alike in their origin. Guano is mainly the excrement of marine birds mixed with the remains of the birds themselves and the fish they have brought to land. In some cases on the Chincha Islands the deposits are from 160 to 180 feet thick. The lower strata of such deposits may be many thousands of years old.

Nowhere else in the world are marine birds found in such vast quantities as along the west coast of South America from Panama south to Chile. The larger number of these birds have their roosts and breeding places on the Peruvian Islands, or on points of the mainland. Their presence in such vast numbers is due to the quantity of fish found along these coasts.

Cormorants, pelicans, sea gulls, marine crows, in flocks numbering hundreds of thousands, may be seen in these regions, while the rainless climate preserves the guano deposited. There are hundreds of bird islands in other parts of the world but the excrement and remains of birds found thereon are not the same as Peruvian guano, although the deposits may possess value for fertilizing purposes. Even with the Peruvian guano, analysis shows great differences.

All excrements contain nitrogen in the form of urates and salts of ammonia, but these are to a large extent lost unless the manure is at once applied to the land and even then the nitrogen may be washed out before it can become available for the plant. When left exposed to a humid atmosphere or when rain is allowed to fall on it, the nitrogen salts are quickly leached out. The Peruvian guano, in its natural state, having seldom been exposed to rain or dampness, has retained its nitrogenous properties, and as it is rich in all three elements of plant food it is more valuable than other guanos.

Guano has been used in Peru for centuries. As early as 1806 it was used in England, and in 1824, fifty vessels loaded annually at Chincha. It was used in the United States as early as 1832. Baron Humboldt in 1804 was the first to make it known to Europeans; its commercial importance there dating from 1844. As before stated, the Chincha Islands were the first exploited. Nine million tons were extracted in ten years. Other deposits were developed in 1870. The Ballesta, Macabi, and Guanape Islands yielded 1,500,000 tons. Next the Lobos Islands were worked as well as the enormous deposits of the Province of Tarapaca on the south coast of Peru. It has been estimated that in forty years over 18,500,000 tons were taken from these localities, or more than 440,000 tons annually.

As the penguins and pelicans are very voracious, each bird is capable of furnishing, on an average, about 32 grams of excrement per night. It is estimated that 100 kilograms of guano, containing 14 per cent of nitrogen and 10 per cent of phosphoric acid, required the consumption of 600 kilograms of fish containing 2.3 per cent nitrogen and 1.7 per cent phosphoric acid. An annual deposit of 40,000 tons is, therefore, the digestive product of 3,420,000 pelicans. It is reported that, while the old beds have been considerably reduced, there are layers 30 feet thick which have not been touched and which are still forming.

The Caribbean deposits are much lower in nitrogen than the Peruvian, but they run very high in phosphoric acid. In these much of the nitrogen has been leached out by the action of rain. The deposits found in the islands of Sombrero, Navassa, Aruba, Curaçao, Orchillas, Roncador, and the Pedro and Morant keys are similar to those found on the Caribbean coast.

The guano is taken out by shovel and pick. As the coasts are rough and few harbors exist, loading of steamers can be done only in calm weather. The water is very deep, and large steamers can anchor close to the shore, so that most of the guano can be loaded directly into the steamer from the shore by means of cable trams. In some cases, it has to be taken to the steamer in small boats. These obviously inefficient and antiquated methods of handling the material can certainly be improved and probably will have to be if guano is to stay in the running as a source of fertilizer.

Dry Fish Scrap—The menhaden (*Brevoortia tyrannus*) belongs to the family Clupeidæ and has many local names. On the Maine coast it is call pogy, bony fish, moss-bunker; in Massachusetts, hardhead bunker; in Delaware, bug fish, in addition to those already given; on the Virginia coast, old wife, cheboy, ellfish, bug fish, green tail, and bughead; in North Carolina, fat-back and yellow-tail shad.

When full grown the fish weighs from 10 ounces to 1½ pounds and measures from 12 to 15 inches in length. They are found in immense schools on the American North Atlantic coast from the Bay of Fundy to the Mosquito Inlet, Florida. Its usual habitat is the bays and rivers, sometimes as far as the brackish water extends, and oceanward as far as to the Gulf Stream. On the approach of warm weather the schools begin to appear and remain until cold weather. Approximately a temperature of 60 to 70° F. appears favorable. In the Chesapeake Bay the season extends from March and April to November and December. The New Jersey fishing season begins about May 1 and ends about the middle of November.

The habit o fthe fish is to congregate in very large schools and then swim along close to the surface of the water, packed closely side by side and tier on tier. As many as 450,000 tons of these fish have been taken in a single season. As soon as the fish appear, steam and sailing vessels start out from the numerous factories along the coast and remain in commission until the fish have disappeared in the fall. In the spring the northern factories send their steamers south and they follow the fish north. In the fall they follow them south again until they get beyond the point where it is economical to fish for them. The average steamers are of about 80 tons burden and usually about 90 feet long; such a vessel will take a cargo of from 250,000 to 300,000 fish. The crew consists of about 17 men. Larger steamers are used by some of the factories and in such cases two seines are carried. These steamers will hold from 900,000 to 1,200,000 fish and have crews of 24 men. The fish are taken in large seines.

When a steamer has a load it returns to the factory, as the fish, if kept too long, soon turn soft and are then very difficult to handle. On reaching the factory, the fish are unloaded by being shoveled into a traveling conveyor which takes them to a belt which carries them into the store shed. From here they are carried to a continuous steam cooker, where the oil cells are broken and the fish bodies broken up. This requires but a few minutes, after which the fish are run into strew presses. On leaving the cookers they contain about 75 per cent of water. The screw presses can press the fish down to about 45 to 50 per cent of water. Most of the oil is liberated here. The water and oil are run into large settling tanks and the oil, which rises to the top, is taken off.

From the presses the fish then go to direct-heat or steam-heated cylindrical dryers. They are dropped into the hot end of the dryer fired with either soft coal or oil. The water in the scrap prevents the burning of the fish. The scrap falls to the bottom of the dryer and is carried around as it revolves, and showered down through the hot gases. On reaching the end of the dryer it is cool enough to handle and contains about 8 per cent water. It is now picked up by a traveling belt and run to the storehouse, where it is bagged, ready for shipment. Great care must be taken in the storeroom, because of the combustible nature of this material, owing to the presence of the oil left in it. It heats very rapidly if left in large piles and must be cooled by turning over.

The capacity of a factory is usually calculated as the number of barrels per day of fish that it can handle. One barrel contains 300 fish. A large and well-equipped factory will handle 700 barrels of fish per hour, turning same out as wet acid scrap, or if the dryer capacity is equal to the cooking and pressing capacity as dry scrap.

To produce one ton of dry scrap requires an average of 50 barrels of fish, while to make one ton of acid scrap (wet) requires 30 barrels of fish. In a good season about 3 gallons of oil per barrel of fish is recovered.

Wet Acid Scrap. Where the plant does not have enough dryer capacity to take care of the catch, the excess is made into wet scrap. The fish scrap from the presses is acidulated with from 60 to 80 pounds 60° Bé. sulfuric acid to the ton of wet scrap. This converts some of the bone phosphate into the available form and at the same time preserves the scrap from decomposition. Good acid scrap that has not lain long in piles will analyze, on 50 per cent water basis, as high as 7.50 to 7.75 per cent ammonia.

In many small factories, hydraulic presses are used instead of screw presses, and the wet scrap is dried in the open air on large wooden drying floors. It must be turned over frequently and this is done by the use of harrows drawn by a horse. It has then to be piled, left to heat to some extent, again spread and turned. If the scrap is wet by a storm, the process has to be repeated. Dry scrap will run about 10 per cent water and 10.50 per cent ammonia, and will still carry 8 to 12 per cent oil.

Leather Scrap and Similar Waste Products—To recover its nitrogenous fertilizer value, leather scrap is treated with steam under heavy pressure, sometimes with the addition of small amounts of sulfuric acid. By this means the nitrogen is rendered highly available, the raw ammoniates obtained containing up to 11 per cent available ammonia. They are sold under various trade names, such as nitrolene, process tankage, agrinite tankage, corona hynite, omega, Rehmsdorf process, Smirow tankage, etc.

The horns and hoofs[7] not available for more valuable purposes are slightly cooked until they become friable and are then ground to a fine powder for use. They run from 4 to 6 per cent water and 15 to 17 per cent ammonia.

Most long hair is used for other purposes than fertilizers, but large numbers

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[7] See also Chapter 43.

of South American hides are imported for making leather and the short hair from these hides, after being removed by the sweating process in tanneries,[8] is utilized as a source of ammonia for fertilizer manufacture. Without treatment, the nitrogenous compounds of the hair are not available for plant food, but during the process of making acid phosphate the hair is subjected to the hydrofluoric acid fumes given off when the phosphate rock is treated with sulfuric acid and becomes decomposed; the sulfuric acid then unites with it and forms ammonium sulfate, thus furnishing available ammonia.

Sewage Sludge—Sewage sludge is now being treated, activated, and used as fertilizer. The city of Milwaukee is marketing a product called Milorganite and in California Nitrorganic is being made by the city of Pasadena.

Cottonseed Meal—The products obtained from the cotton seed are lint, oil, hulls, and meal. Only the meal is used in the manufacture of fertilizers. It is obtained by grinding the cake which is left after the oil has been pressed out. Its chief uses are as a cattle food and as fertilizer. Meal which has been damaged by being overheated can be used only for fertilizer purposes.

The plant food in cottonseed meal is chiefly nitrogen, so that its fertilizing value depends upon the quantity of nitrogen present. It contains, however, an appreciable amount of phosphoric acid and potash. An average analysis is as follows:

	Per Cent
Nitrogen	6.79
Phosphoric acid	2.88
Potash	1.77

In using cottonseed meal as a fertilizer it must be borne in mind that it is essentially a nitrogen provider, hence if the soil requires phosphoric acid and potash in any appreciable quantities as well as the nitrogen, the meal should be used in connection with some form of fertilizer furnishing these other materials.

Calcium Cyanamid—The cyanamid process for the fixation of air nitrogen was discovered in 1898 but it was not until 1906 that the first large producing unit was built at Piano d'Orta, Italy. From this small beginning the production has risen to well over 1,500,000 tons per annum. The largest plant in the world is at Niagara Falls on the Canadian side.

Briefly, the manufacture[9] consists in passing purified nitrogen (from the air) over calcium carbide held at a temperature of 2000° F. in cylindrical fixation ovens. When the reaction is completed, the mass is cooled and pulverized. Water is then added to decompose any free carbide and to hydrate the lime. To prevent dust, 4 per cent of oil is added to the pulverized material.

The grade used as a fertilizer has the following approximate composition:

	Per Cent
Calcium cyanamid ($CaCN_2$)	63.00
Calcium hydroxide ($Ca(OH)_2$)	17.00
Free carbon	12.00
Limestone impurities	4.00

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[8] See Chapter 45.

[9] For details of the manufacture, see Chapter 8.

Since 1932, the bulk of the material manufactured at Niagara Falls has been converted into a granular form by omitting the oil and mixing in a binding material and then granulating. This is graded between 12 and 100 mesh with not over 2 per cent passing the 100 mesh.

When mixed with moist soil, calcium cyanamid changes to calcium hydroxide and urea, $NH_2 \cdot CO \cdot NH_2$. This calcium hydroxide, plus that present as such originally in the cyanamid, gives it a lime value equivalent to 70 per cent hydrated lime.

About 75 per cent of the world production is used in the fertilizer trade; the greater proportion as a single fertilizer material applied directly to the soil. In addition to supplying nitrogen to the soil it has a number of other valuable features. If it is broadcast and plowed under with cover crops it aids very materially in the production of humus and if used in amounts of 1000 pounds per acre or even more, will kill all weeds and render the soil practically sterile. When so used, sufficient time must be allowed for the cyanamid to thoroughly decompose before planting.

Other Sources of Nitrogen Fertilizers—The other principal sources of nitrogen compounds for fertilizer are: Chile saltpeter ($NaNO_3$), synthetic ammonia and ammonium sulfate from the distillation of coal in by-product coke ovens. The production of these materials is discussed in other chapters.[10]

POTASH IN THE FERTILIZER INDUSTRY

It has become customary to speak of the potassium content of fertilizers and fertilizer materials in terms of potassium oxide and to use the word "potash" to represent this compound in all the forms in which the element potassium is used in agriculture. The chemist's designations "potassium chloride," "potassium sulfate," and "potassium oxide" are more familiar in the fertilizer industry as "muriate of potash," "sulfate of potash," and "K_2O," respectively. Because of the solubility of its compounds, potassium is an element which is removed in great quantities from the soil. Table 1 shows the potash removal[11] by some important crops.

TABLE 1—POTASH REMOVAL BY CROPS

Crops	*Yield/Acre*	*Potash Removed (Lbs. K_2O)*
Alfalfa	4 tons	178.4
Clover hay	2 tons	65.2
Corn	75 bu. (plus stalks)	82.8
Cotton	600 lbs. lint (entire plant)	59.6
Oats	50 bu. (plus straw)	40.8
Potatoes	300 bu.	95.0
Rye	35 bu. (grain)	40.0
Soybeans	25 bu. (beans)	86.0
Sugar beets	10 tons (beets)	64.0
Tobacco	1000 lbs. leaves (plus stalks)	78.0
Wheat	30 bu. grain (plus straw)	25.2

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[10] Chile saltpeter, Chapter 9; synthetic ammonia, Chapter 8; ammonium sulfate from coal, Chapter 15.

[11] Lodge, F. S., Chem. Met. Eng., *30*, 879 (1938).

It has been estimated that harvested crops in the United States remove annually over 3,500,000 tons of potash from the soil. In addition, there is some loss by leaching and soil erosion. Addition of potash to the soil in the form of fertilizers returns only a fraction of that which is removed.

Under some harvesting practices a considerable portion of the potash removed from the soil by the crop while growing is returned to the soil in such crop residues as the straw of cereals and the stalks of cotton.

The Role of Potassium in Plant Life[12]—Up to the present time, even though many physiological studies have been made on this element, there seems to exist little definite evidence indicating the nature of the mechanism by which potassium functions. It has a specific role in influencing the absorption of certain other mineral elements, in assimilating carbon, in translocating sugars and forming starch, in regulating the rate of respiration, and also in influencing the action of enzymes.

Obviously potassium is essential in all cell metabolic processes. When deficiencies in the soil supply of available potassium occur, changes in these physiological processes may result. Foliage discolorations, necroses of various kinds, and greater susceptibility to fungous diseases are manifestations of this deficiency. These various injuries reduce yields and quality of the plant products and serve to emphasize the important role of potassium in plant metabolism.

Potash Production[13]—The manufacture of potash fertilizers consists in mixing potassium salts with a filler to produce a fertilizer containing the desired potash (as K_2O) content. Potash raw materials are roughly divided into two classes—those consisting largely of chloride salts and those relatively free from chlorine. Potassium chloride is by far the leading potassium-containing raw material. Potash production thus usually involves the separation and refinement of this salt from its natural deposits. However, the quality of certain crops is adversely affected by too much chloride. Tobacco is a notable example. Therefore, other potash raw materials are sometimes desirable. In this case the potash raw material may be potassium sulfate (K_2SO_4), magnesium potassium sulfate ($MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$), potassium nitrate ($KNO_3$) or carbonate ($K_2CO_3$).

The story of the growth of the American potash industry, following the World War I disclosure of our unhealthy dependency on Germany for potash salts, is one of industrial romance. Discovery of potash deposits in California, Texas, and New Mexico made possible the growth of a domestic potash industry.[14] From a beginning in 1915 of only a thousand tons of potassium oxide this industry has been developed until now production is approximately one-half of our consumption. Should the necessity arise, present operators could in a short while supply all of our needs.

PHOSPHATE FERTILIZERS

Phosphorus compounds must be added to the soil in larger proportions than any other fertilizer constituents, largely because of their limited solubility.[15] The principal source of the very large tonnage required is the phosphate rock

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[12] Hoffer, G. N., Chem. Met. Eng., *30*, 885 (1938).

[13] For figures on production and consumption of potash see Chapter 9.

[14] Symposium on Potash, Chem. & Met. Eng., *30*, 853-78 (1938).

[15] See p. 516.

($Ca_3(PO_4)_2$), which is found widely scattered throughout the world. The principal phosphate workings today are to be found in Florida, South Carolina, and Tennessee in the United States, in Algeria and in the Ocean and Christmas Islands in the Far East.

Phosphate Mining—The first serious attempt to obtain phosphate on this continent was in Canada, mining Canadian apatite. This is a very high-grade material, but it was very expensive to mine and when, in 1870, the South Carolina, and, in 1888, the Florida deposits were marketed, it could not compete with them. The rock in South Carolina is found in two grades—river and land pebble. It is deposited in considerable quantities along the margins of navigable streams and in the river beds between Charleston and Beaufort. The rock of Northern Africa, on account of its locality, is consumed entirely in Europe, and the production of the East Indies finds its market in Japan and Australia as well as in Europe.

Florida Phosphate—In 1889 pebble phosphate was discovered in De Soto County. Several months later land rock phosphate was uncovered at Dunellon in Marion County. This is the most valuable of the Florida phosphates and its discovery at once caused the investment of large amounts of capital. In the following year plate rock phosphate was discovered at Anthony in Marion County. Land rock phosphate is unlike the river and land pebble phosphate. The deposits in Florida are as a rule about 175 by 15 miles in area, parallel with the coast, and about 20 miles inland. Plate rock phosphate is mined only in a limited section of Marion County. It acts as a covering for limestone cones and is from 6 inches to 1 foot in thickness.

Pebble rock phosphate is almost entirely of marine formation and is located in the beds of small rivers and lakes and in areas originally covered with water. It is found far back from the coast in areas about 20 by 60 miles in extent and in tonnage produced surpasses both land and plate rock. Pebble rock occurs in the form of rounded pebbles varying up to a size somewhat smaller than a hen's egg.

Hydraulic mining is employed. Powerful streams of water are thrown against the edge of the bed and the phosphate gravel, together with the sand and clay, is washed into a hole about 10 feet in diameter and 10 to 15 feet deep. The gravel is sucked up from this hole through a pipe and run to the mill, which may be half a mile or more away. Here it is passed over screens which allow the fine silt and sand to escape while the phosphate pebbles are caught; this serves to wash the rock. It is then passed through direct-heat rotary dryers and carried by belts to the storage bins, ready for shipment.

Another method of mining this rock is by means of dredges which scoop the rock from the bottom of the river or lake and dump it into cars which carry it to the mills. In some cases suction dredges are used, a partial separation of the rock and clay being made on the dredge, the rock being dumped into cars and the sludge thrown out.

The bulk of the land pebble runs from 68 to 70 per cent *bone* phosphate, while high-grade hard rock runs 76 to 78 per cent. The iron and alumina content is about 2 to 3 per cent.

Tennessee Brown Rock Phosphate—The Tennessee phosphates occur almost entirely in Silurian and Devonian strata, but more particularly in the former, and in the transition strata between the two. In December, 1893, blue rock phosphate was discovered in Hickman County. The beds of brown rock in this vicinity, which are the finest phosphate deposits in the world, were not worked till later. Some 45,000,000 tons of this brown rock are estimated as being available for mining in this district. New fields are being continually opened up, railroads built and large quantities shipped. As the brown rock of this locality is gradually used, the vast blue rock fields of Maury, Hickman, and Lewis Counties will come into active development.

This brown rock lies in strata formation with layers of clay and earth as overburden. This overburden is stripped by hand or steam shovel and the soft wet phosphate taken out either by hand or steam shovel. It is carried to the washers, where it is freed from most of the clay and dirt. On account of the porous nature of this rock, the clay is disseminated all through it and it is very difficult to get rid of all the clay by the use of simple log washers. Many types of washers are used, the most efficient being the form used in cleansing glass-maker's sand. The washing is accomplished by pumping the fine material through pipes having sharp angles, where the pressure is greatly increased. The clay is washed out in this manner and the clean rock is finally delivered to very deep settling tanks where the muddy water holding the clay in suspension is drawn off. The heavier rock which settles, after the tank is filled, is dried in rotary direct-heat dryers and is then ready for shipment. This method cleans the rock thoroughly.

Much of the material that is washed in log-washers or by use of revolving screens is more thoroughly cleansed of the adhering clay by blowing a very strong blast of air through the direct-heat dryers, thus blowing off the lighter dust, or floats. This gives a fairly good material, but the loss in phosphate is rather large, as the floats will test from 50 to 60 per cent bone phosphate. It is very important to reduce the clay as much as possible, as well as the iron and aluminum phosphate, as these prevent the making of high available acid phosphate.

This brief discussion of handling and washing of the Florida and Tennessee brown rock phosphates indicates the methods of mining and washing used. With some modification these methods are used for all the phosphate deposits.

Phosphate deposits of greater or less importance are widespread throughout the United States. Tennessee has other extensive deposits known as Tennessee blue rock and Tennessee white rock phosphate. Much of the research and development work of the Tennessee Valley Authority has been concerned with producing higher grade fertilizer material from the Tennessee phosphate deposits. South Carolina has extensive phosphate deposits which are worked commercially. There are vast deposits of phosphate rock in Idaho that are as yet worked to only a limited extent because the principal fertilizer market is too distant.

Phosphates in the South Seas—The islands of the Pacific Ocean contain some of the largest known deposits of high-grade phosphates. The deposits in Ocean and Pleasant Islands in the Gilbert group are estimated at 50,000,000 tons. About 300,000 tons yearly is being mined and shipped. About 100,000 tons is taken to Japan, 80,000 to Australia, and the remainder to Europe. Europe also receives yearly about 100,000 tons from Christmas Island. Good grade phosphate has been found on the islands in the French colony of Tahiti and dependencies. These islands, Makatea, Matahiva, and Niau, lie in the northwestern part of the

Tuamotu Archipelago. The high-grade deposits in Makatea are estimated at 10,000,000 tons, with many million more tons of lower grade. These deposits range from 73 to 80 per cent *bone* phosphate content. It is estimated that when the works are completed and working at full capacity 200,000 tons yearly will be shipped. This island, together with the island of Angaur, about 600 miles to the east of the Philippine island of Mindanao, is a coral island and has been for ages the resort of countless flocks of marine birds. Their excrement accumulated in vast quantities, but was not preserved unchanged as is the case in the guano islands. The heavy rains of this section of the Pacific caused a steady leaching of the soluble phosphates, which, coming in contact with the porous coral growth beneath of pure calcium carbonate, gradually changed it into calcium phosphate.

Chemistry of the Manufacture of Acid or Superphosphate—The reaction which takes place on the addition of sulfuric acid to phosphate rock or bone is as follows:

$$3Ca_3(PO_4)_2 + 6H_2SO_4 + 12H_2O = 4H_3PO_4 + Ca_3(PO_4)_2 + 6CaSO_4 \cdot 2H_2O$$

and

$$4H_3PO_4 + Ca_3(PO_4)_2 + 3H_2O = 3CaH_4(PO_4)_2 \cdot H_2O.$$

A simpler form of the reaction is expressed as follows:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O = CaH_4(PO_4)_2 \cdot H_2O + 2CaSO_4 \cdot 2H_2O.$$

If 310 parts by weight of finely ground tricalcium phosphate is mixed with 196 parts of sulfuric acid and 90 parts of water, and the resulting jelly is quickly diluted with water and filtered, there will be found in the filtrate about three-quarters of the total phosphoric acid as free acid. If, however, the jelly is left to become dry and hard, the filtrate, when the mass is beaten up with water and filtered, will contain monocalcium phosphate, $CaHPO_4$.

If the quantity of sulfuric acid used is not sufficient for complete decomposition, the dicalcium salt is formed directly according to the following reaction:

$$Ca_3(PO_4)_2 + H_2SO_4 + 6H_2O = 2CaH(PO_4) \cdot 2H_2O + CaSO_4 \cdot 2H_2O.$$

This arises doubtless by the formation at first of the regular monocalcium salt and the further reaction of this with the tricalcium compound as follows:

$$CaH_4(PO_4)_2 + H_2O + Ca_3(PO_4)_2 + 7H_2O = 2Ca_2H_2(PO_4)_2 \cdot 4H_2O.$$

This reaction represents, theoretically, the so-called reversion of the phosphoric acid. When there is an excess of the sulphuric acid, there is a complete decomposition of the calcium salts with the production of free phosphoric acid and gypsum. This reaction is represented as follows:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O = 2H_3PO_4 + 3(CaSO_4 \cdot 2H_2O).$$

Reactions with Fluorides. Since calcium fluoride is present in nearly all mineral phosphates, the reactions of this compound must be taken into consideration in the chemistry of this subject. When treated with sulfuric acid the following reaction takes place:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

The free HF then reacts with any silica present as follows:

$$4HF + SiO_2 = 2H_2O + SiF_4.$$

This compound, however, is decomposed at once in the presence of water, forming hydrofluosilicic acid, as follows:

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6.$$

The presence of fluorides is very objectionable both on account of the dangerous gases evolved during the manufacture and because 100 lbs. of calcium fluoride will consume 125.6 lbs. of the sulfuric acid.

Reaction with Carbonates. Most mineral phosphates contain carbonates in varying quantities. On treatment with sulfuric acid these are decomposed as follows:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2.$$

When present in only moderate quantities they are not objectionable, as the reaction produces a rise in temperature and the CO_2 formed permeates and lightens the whole mass, thus assisting in completing the reaction by leaving the mass porous, and capable of being easily dried and pulverized. When large quantities are present, however, additional water should be added to furnish the proper amount for the crystallization of the gypsum.

Solution of the Iron and Alumina Compounds. Iron may occur in mineral phosphates in many forms. It probably is most frequently present as ferrous or ferric phosphate, seldom as oxide, but often as pyrite. The alumina is chiefly present as phosphate and as silicate. When, as is generally the case, a little less sulfuric acid is employed than is necessary for complete solution, the iron phosphate is attacked as follows:

$$3FePO_4 + 3H_2SO_4 = FePO_4 \cdot 2H_3PO_4 + Fe_2(SO_4)_3.$$

A part of the iron sulfate formed reacts with the acid calcium phosphate present to produce a permanent jelly-like compound, difficult to dry and handle. By careful control as much as 4 to 6 per cent may be handled, but over 2 per cent is objectionable. Pyrite and silicate are not attacked by dilute sulfuric acid so these compounds are not objectionable and no account is taken of them in analyzing phosphates.

With sufficient acid aluminum phosphate is decomposed with the formation of aluminum sulfate and free phosphoric acid, as follows:

$$AlPO_4 + 3H_2SO_4 = Al_2(SO_4)_3 + 2H_3PO_4.$$

Reaction with Magnesium Compounds. The mineral phosphates, as a rule, contain but little magnesia. When present it is probably as an acid salt, $MgHPO_4$. Its decomposition takes place in slight deficiency or excess of sulfuric acid respectively as follows:

$$2MgHPO_4 + H_2SO_4 + 2H_2O = (MgH_4(PO_4)_2 \cdot 2H_2O) + MgSO_4$$

and

$$MgHPO_4 + H_2SO_4 = H_3PO_4 + MgSO_4.$$

The magnesium, when present as oxide, is capable of producing a reversion of the monocalcium phosphate as follows:

$$CaH_4(PO_4)_2 + MgO = CaMgH_2(PO_4)_2 + H_2O.$$

This renders the phosphate less soluble. Hence, magnesium is an undesirable constituent of phosphate rock.

Double and Treble Superphosphate—From the equations given above, it can be seen that the "available" phosphate in the ordinary superphosphate is only a small proportion of the total weight because of the presence of gypsum ($CaSO_4 \cdot 2H_2O$) formed by the reaction. The available phosphate in commercial superphosphate is usually of the order of 20 per cent. To increase the fertilizer value of phosphate there is an increasing trend toward the production of "double" and "treble" superphosphate. In the older method, phosphâte rock is first treated with sulfuric acid with the formation of phosphoric acid and gypsum as shown in the above equations. The gypsum is separated by filtration and the phosphoric acid is used to treat a second lot of phosphate rock, thus forming superphosphate of 40 to 50 per cent available phosphoric acid content as per the following equation:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2.$$

More recently there has been a great increase in the production of pure phosphoric acid by the oxidization of elemental phosphorus to phosphorus pentoxide, which is absorbed in water. The elemental phosphorus is produced in blast furnaces or electric furnaces.[16]

Other Sources of Phosphate—*Thomas or Belgian Slag.* Thomas or basic slag is a by-product in the modern method of steel manufacture[17] from pig iron containing appreciable quantities of phosphorus. The process of removing the phosphorus from the pig iron was first discovered by the English engineers Gilchrist and Thomas and consists in adding to the Bessemer converter containing the molten pig iron a definite quantity of freshly burnt lime, which after powerful reaction, unites with the phosphorus and floats on the top of the molten steel in the form of a slag.

The fertilizer value of the slag was not recognized for a long time. A considerable portion of its phosphoric acid was found to be soluble in dilute citric and carbonic acids, which led to successful field experiments. The only preparation of the slag for fertilizer purposes when its value was first recognized, consisted in having it finely ground in specially prepared mills so that 75 per cent would pass a sieve of 0.17 mm. mesh.

The form in which the phosphoric acid exists in the slag has never been fully explained. It was formerly supposed that it was combined with lime as a tetracalcium phosphate and that this latter compound being less stable than tricalcium phosphate, under the influence of dilute acids became easily available to the plants by being decomposed into the calcium salt of the dissolving acid, and tricalcium phosphate. The tetracalcium phosphate, however, has never been made artificially, although it has been recognized under the microscope in the

[16] Killeffer, D. H., Ind. Eng. Chem., *30,* 967 (1938); Kirkpatrick, S. D., Chem. & Met. Eng., *44,* 644 (1937); Chem. & Met. Eng., *46,* 269 (1939).

[17] See Chapter 23.

slag and exists as a mineral under the same name of Isoklas. It is now generally held that the phosphoric acid is combined in the slag as a double salt of tricalcium phosphate and calcium silicate and that in this form the roots are able to utilize it. It is also believed that some of the phosphoric acid is more or less united with iron as a basic iron phosphate.

Bone. Bones consist of two distinct kinds of matter. One is mineral in character and consists of phosphate of lime or true bone phosphate; the other is organic, consisting of a flesh-like matter called ossein, which contains much nitrogen.

Bones as a source of phosphates for fertilizer manufacture come on the market in several forms. In large packing houses or in localities where large amounts of bone can be collected, they are treated for the extraction[18] of gelatin. To extract the gelatin, the bones are steamed in tanks under 40 lbs. pressure for three or four hours. The gelatin is dissolved and the liberated grease rises to the top. The bones, with some meat still adhering, are removed from the tanks, dried and ground, producing "steamed bone meal." This contains from 4 to 4½ per cent ammonia and 22 to 24 per cent bone phosphate. If steamed at a pressure of 50 to 60 pounds and for a longer time, more of the gelatin is removed and the meal runs correspondingly lower in ammonia. Raw bone is bone that has been boiled in open kettles to remove the grease and gelatin. This method, however, is not as efficient as steaming under pressure and the bone meal runs higher in ammonia and lower in phosphoric acid.

Bone Black. For use in sugar refining,[19] bones are calcined until black and brittle. This removes all the organic matter and renders them very porous. After their value to the sugar refiner is gone, they are sold to the fertilizer manufacturer as bone-black, containing about 30 to 35 per cent phosphoric acid and no ammonia.

Part of the phosphoric acid in steamed or raw bone meal is in the available form. This class of bone is a very good fertilizer material as the phosphoric acid is decomposable in the ground and in the course of four or five years is rendered completely available, thus furnishing a steady supply of phosphoric acid to plant growth. The phosphoric acid of bone-black or bone ash is, however, unavailable without treatment with acid. Superphosphate and dissolved bone-black are terms applied to the bone meal and bone-black which have been acidulated so that the phosphoric acid is rendered available for plant growth.

THE MANUFACTURE OF FERTILIZERS FROM WASTES

Slaughter House Tankage—In all slaughter houses the scrap meat is saved and treated for the production of "tankage." As all this material has more or less grease still adhering to it, it is first placed in large tanks and boiled under pressure till the grease has left the meat and the bone. The scrap is then allowed to drop to the bottom of the tank and the liquor is drawn off into large vats. After the grease has risen to the top it is withdrawn. The remaining liquor is then treated for its fertilizing constituents as given elsewhere under "concentrated tankage."

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[18] See Chapter 43.
[19] See Chapter 35.

The scrap meat and bone, or as it is called, "tankage," is now pressed to free it as much as possible from the water and adhering grease and is then dried in rotary direct-heat or steam dryers. It is then ready for sale.

In plants where the liquors are evaporated for "concentrated tankage" it is general practice to mix the "stick" or thick liquor obtained by evaporation directly with the tankage before drying. This raises the percentage of ammonia and at the same time does away with the making of a second product.

There are several grades of tankage made, depending on the quantity of bone present. In small plants practically all the bone, except the very largest pieces, are left with the tankage. This gives a product running low in ammonia and high in bone phosphate. Such tankage may run from 5 to 8 per cent ammonia and up to 25 to 30 per cent bone phosphate.

In the larger plants, such as the Chicago packing plants, more care is taken to remove the bone, thus giving a tankage of higher ammonia content and lower bone phosphate. This will run about 11 per cent ammonia and 15 per cent bone phosphate.

There are three usual grades of tankage quoted in daily market reports as follows:

11 per cent ammonia and 15 per cent bone phosphate,
10 per cent ammonia and 20 per cent bone phosphate, and
9 per cent ammonia and 20 per cent bone phosphate.

The steaming, pressing, and drying do not remove all the grease. The best that can be done is to get it down to 6 to 8 per cent on the basis of the dried material, while frequently, where factory practice is bad, it will run as high as 20 per cent. This, of course, lowers the percentage of both ammonia and bone phosphate. As the grease balls the material and makes it hard to grind, its presence in large quantity leaves the tankage in bad condition for making into complete fertilizer. Where the fire hazard is not too great, and the plant is large enough, naphtha extraction is used to remove this grease from the dried tankage. Frequently in neighborhoods where a centrally located plant can obtain tankage from a number of small packing houses, naphtha extraction is employed, so that the grease and the grease-free tankage may be obtained. The grease is removed in these plants by subjecting the tankage to the solvent action of naphtha under pressure in large tanks holding from 10 to 20 tons of tankage. After a number of hours' treatment, the temperature is reduced and the naphtha withdrawn. Live steam is then blown in to remove the excess of naphtha, the tankage finally withdrawn and spread over a large area to let the remaining naphtha evaporate. This process will remove all but 1 or 2 per cent of the grease.

Garbage Reduction—The garbage is collected in wagons which have watertight steel bodies and sectional canvas covers. It is hauled to the central loading station and dumped into the garbage cars.

The garbage when delivered is weighed on railway track scales and then run into the green garbage building, Figure 1, on a siding which extends through it. The free water is drained off through a gutter extending the full length of the building. The swill water from the gutter is drained into a catch-basin, from which it is discharged into the grease separating tanks, after which it is evaporated.

The essential operation in treating the garbage consists of cooking in large digesters for about 6 hours with live steam at 60 to 70 lbs. gage pressure. After discharging from the digesters, the grease floats on the surface of the water and is skimmed off and sold separately. The water, containing dissolved solids, is fed to triple effect evaporators, thus concentrating the dissolved solids. This concentrated solution is mixed with the solids from the digesters and the mass is dried in cylindrical or vacuum driers.

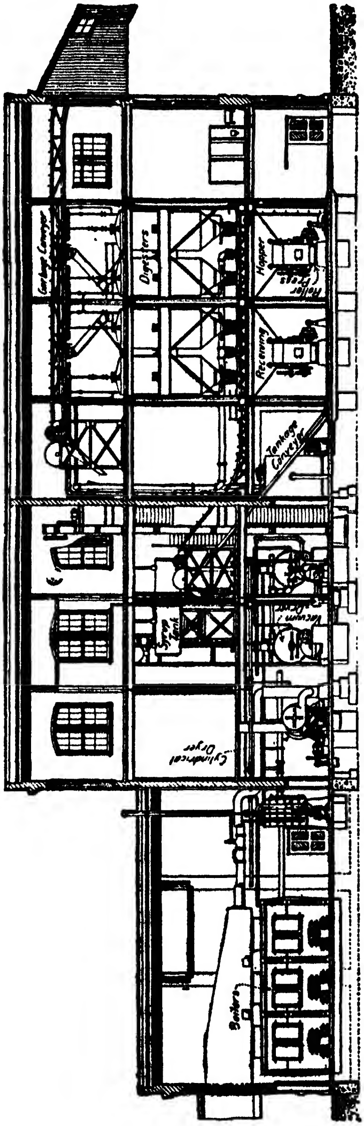

FIG. 1. Garbage Reduction Plant.

SPECIAL SYNTHETIC FERTILIZER MATERIALS

Several "made to order" synthetic fertilizers have been developed. These have as their main purpose the concentration in definite proportions of certain desired quantities of nitrogen, phosphoric acid, and potassium. They represent only some 2.5 per cent of the total fertilizer tonnage used, but since they are of interest in certain cases, a listing of the more recent developments is presented.

Ammo-Phos—2 grades. 13 per cent ammonia and 48 per cent available phosphoric acid, and 20 per cent ammonia and 20 per cent available phosphoric acid.

Calurea—Combination of synthetic urea and calcium nitrate containing 34 per cent nitrogen, 20 per cent as nitrate nitrogen and 80 per cent as urea nitrogen.

Kaliammonsaltpeter — Potassium chloride and ammonium nitrate mixed with water and dried.

Leunaphoska—Mixture of di-ammonium phosphate, potassium chloride, and ammonium sulfate. Contains 16 per cent ammonia, 13 per cent phosphoric acid.

Leuna Saltpeter—Double salt of ammonium sulfate and nitrate, containing about 31 per cent ammonia, one-fourth as nitrate and three-fourths as ammonium salts.

Nitrophoska—Made from di-ammonium phosphate, ammonium nitrate and potash salts in various grades according to nitrogen, phosphoric acid, and potash content desired.

Phosphazote—Cyanamid is converted into urea by sulfuric acid and the acid neutralized with phosphate rock.

Urea—Synthetic urea containing about 46 per cent ammonium nitrate and limestone containing about 20 per cent nitrogen and 36-40 per cent limestone.

Manganese Sulfate—Some soils, particularly those of an alkaline nature, are lacking in manganese. Hence manganese sulfate has entered into the field of special fertilizers.

METHODS OF GROWING PLANTS IN SOLUTION AND SAND CULTURES

In order to study under accurately controlled conditions problems relating to the nutrition of plants, experiments are now being carried on by growing plants in solution and sand cultures. A medium grain sand that will allow good drainage and yet is fine enough to hold the solution, is either heated or washed with water hot enough to kill all plant life present. The seed is then sown in the usual manner and the sand kept wet with a chemical solution containing all the elements needed for perfect growth of the plant. In this way, in addition to the three well known elements, nitrogen-phosphorus acid and potassium, additions of compounds of other elements in minute amounts must be made. It has been found that such elements as copper, zinc, manganese, boron, etc., though present in only a few parts per million, are very essential to the perfect development of the plant. Of course it is necessary also that calcium, magnesium and sulfur be present but these are found in the materials furnishing the nitrogen, phosphoric acid and potash.

The following formula is well adapted for general use.

Monopotassium phosphate . . .	5.90 grams	per 5 gallons of solution
Calcium nitrate	20.10 grams	
Magnesium sulfate (crys.)	10.70 grams	
Ammonium sulfate	1.80 grams	

Each material is dissolved in a pint of water and then added to four gallons of water in a stock bottle and the solution made up to 5 gallons. To this stock solution are now added not more than 10 cc. of a stock solution of trace elements prepared by dissolving together in a pint of water 0.80 grams each of boric acid crystals, manganese sulfate and zinc sulfate. As iron is necessary to prevent chlorosis this must also be added, but as iron sulfate slowly precipitates on standing, it should not be added to the stock solution until just before use. A stock solution is made by dissolving 0.80 grams iron sulfate in a pint of water and to each quart of solution as used, 5 cc. of this iron solution is added.

A great deal of experimentation and development will be required before it can be determined whether there will be economic justification in the large scale use of this technique of soilless growth of plants. Though very great growths and yields can be obtained on small areas by this method, success is dependent on very careful, expert control of the conditions of the solutions. The fields where economic success might be expected would be in greenhouse culture and then in market gardening in areas where land values are very high. It is obvious that the use of artificial fertilizers would reach the highest possible efficiency in this method, for there is no loss by leaching or erosion.

THE ECONOMICS OF THE FERTILIZER INDUSTRY

The American fertilizer industry started quite modestly at about the middle of the 19th century when a few plants along the Atlantic seaboard turned out several hundred tons of mixed fertilizers. Production increased steadily until 1900 when the industry produced some 2,500,000 tons of mixed fertilizers. Since then, fertilizer production has on the average kept up with increasing fertilizer sales. Figure 2 shows the trends of fertilizer consumption for the past 40 years. For the past few years consumption has fluctuated between 7,000,000 and 8,000,000 tons annually.

TABLE 2—FERTILIZER MATERIAL USED IN UNITED STATES,[20] FERTILIZER YEAR 1939-40

(Short tons: Estimates by Synthetic Nitrogen Products Corp., for continental U. S. only)

	Total Material	*Plant Food*			*Applied * Directly*
		N	P_2O_5	K_2O	
Sulfate of ammonia	513,000	105,600	......	......	158,000
Nitrate of soda	748,000	120,200	......	......	648,000
By-product ammonia liquor	35,000	7,500	......	......	......
Synthetic N-containing solutions	85,000	38,000	......	......	3,000
Cyanamide	138,000	29,800	......	......	83,000
Calcium nitrate and urea fertilizers	88,000	21,100	......	......	28,000
Imported complete fertilizers	2,000	300	400	400	......
Ammonium phosphates	67,000	8,800	22,700	......	27,000
Nitrate of potash, nitrate of soda-potash	46,000	6,400	......	7,300	21,000
Other potash materials	770,000	......	......	373,000	110,000
Cottonseed meal	135,000	8,100	3,200	2,300	85,000
Other natural organics	660,000	32,300	26,000	5,300	160,000
Bulk superphosphate	3,355,000	......	630,200	......	† 765,000
Basic slag	35,000	......	3,500	......	35,000
Bones, bone meal	92,000	2,100	22,100	......	60,000
Ground phosphate rock	140,000	......	5,600	......	90,000
Sulfuric acid (for acidulating certain organics)	5,000	......	......	......	......
Wood, beet root ashes	9,000	......	......	400	5,000
Dolomite, limestone	350,000	......	......	......	......
Calcined kieserite and other secondary plant food materials	7,000	......	......	......	......
Filler	548,000	......	......	......	......
Total tonnage	7,828,000	380,200	713,700	388,700	2,278,000

* Materials not used in mixed fertilizers; includes materials used in home-made mixtures except liming materials.

† Includes about 20,000 tons of "basic lime phosphate." Does not include triple super distributed by T. V. A. and A. A. A.

In general, the trends of this industry are those which are typical of chemical industry. Consumption has increased irregularly but there was a trend toward

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[20] Chem. & Met. Eng., *48,* 95 (1941).

higher plant food content and also toward the use of more concentrated materials. Meanwhile the price per unit of plant food dropped markedly in recent years. At present, domestic capacity for all fertilizer chemicals is on the increase, including phosphorus and phosphoric acid, ammonia, and potash.

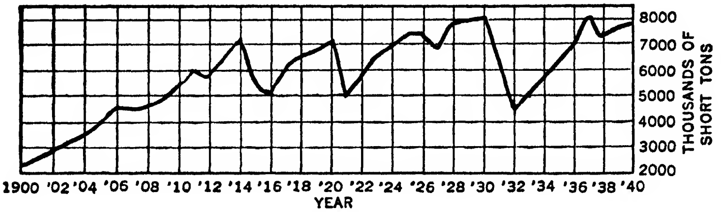

Fig. 2. Fertilizer Sales in the United States.

The fertilizer industry now produces annually products valued at some $170,000,000. In 1940 the commercial fertilizer marketed was slightly more concentrated than ever before, averaging about 19.6 per cent of plant food in all complete mixed goods used. This concentration compares with 19.3 per cent in 1939, and an average of about 16 per cent during the decade beginning 1920.

TABLE 3—VALUE OF FERTILIZERS USED IN UNITED STATES[21]

	1939	*1937*
Fertilizers, aggregate value	$161,887,134	$173,617,111
Complete fertilizers, tons	5,088,468	5,680,619
Value	$117,666,262	$128,750,181
Potash superphosphate, tons	233,355	225,589
Value	$ 4,824,707	$ 4,458,662
Superphosphate, not ammoniated,* total production, tons†	4,152,269	5,275,710
Made for sale, tons	2,756,967	3,112,563
Value	$ 23,937,497	$ 27,846,266
Made and consumed, tons	1,395,302	2,163,147
Bone meal, tons	62,004	84,913
Value	$ 1,760,942	$ 1,919,503
Ammoniated superphosphates, tons	32,878	45,352
Value	$ 572,756	$ 700,842
Other ammoniated fertilizers, tons	6,834	7,734
Value	$ 138,678	$ 114,112
Other fertilizers,‡ tons	360,146	218,844
Value	$ 6,660,877	$ 4,998,520
Tankage, tons	225,575	179,715
Value	$ 6,325,415	$ 4,829,025

* Basis 16 per cent available phosphoric acid.

† In addition, 68,926 tons of superphosphate, basic 47 per cent P_2O_5, was produced by the Tennessee Valley Authority during the fiscal year ended June, 1939.

‡ Includes legume inoculants.

It is estimated that farmers paid approximately $27.75 per ton at the farm in 1940 for fertilizer. During the ten years beginning 1921, the average price was almost $31.

Tables 2 and 3 indicate the present size of the fertilizer industry as well as the relative importance and value of the various fertilizer materials. The striking features of the data are; a large number of different items are used for fertilizer

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[21] Chem. & Met. Eng., *48,* 114 (1941).

and the bulk of them are direct products of chemical industry, rather than natural organic materials.

The increasing importance of chemical industry in the picture is indicated by Table 4, which shows the sources of the nitrogenous materials. The natural organic material (guano, tankage, garbage, etc.) represents much less than 10 per cent of the total nitrogen supply. Though natural organics represent only

TABLE 4—SOURCES OF NITROGEN MATERIALS IN THE UNITED STATES,[22] FERTILIZER YEAR 1939-40

(*Estimates by Synthetic Nitrogen Products Corp.*)

Supplies (without stocks on hand)	*Equivalent Short Tons of Nitrogen*
Domestic production	
At by-product plants	159,900
At synthetic plants	247,500
Sub-total	407,400
Imports	
Sulfate of ammonia	21,200
Chilean nitrate (soda and soda-potash)	118,300
Cyanamide	35,500
Other imports of chemical origin	24,000
Sub-total	199,000
Natural organics (as far as used for fertilizer purposes)	42,500
Grand total	648,900

TABLE 5—CONSUMPTION OF NATURAL ORGANICS FOR FERTILIZER PURPOSES IN CONTINENTAL UNITED STATES,[23] 1939-40

(*Source: Synthetic Nitrogen Products Corp.*)

Materials	*Short Tons of Material*	*Short Tons of Nitrogen*
Cottonseed meal	135,000	8,100
Other seed meals	20,000	1,000
Process tankage	100,000	8,400
Animal tankage	40,000	3,000
Fish scrap and meal	80,000	6,400
Dried blood	10,000	1,300
Garbage tankage	60,000	1,700
Sewage sludge	100,000	4,600
Guano	6,000	500
Castor and tung pomace	15,000	800
Cocoa and other shells	25,000	600
Various rough ammoniates	10,000	600
Dried manure	60,000	800
Bones and bone meal	80,000	2,000
Bone black, dissolved	8,000	100
Tobacco stems	80,000	1,600
Peat	50,000	1,000
Totals	879,000	42,500

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[22] Chem. & Met. Eng., *48*, 96 (1941).
[23] Chem. & Met. Eng., *48*, 97 (1941).

a small part of the commercial fertilizers, the sources are widespread and varied as shown in Table 5.

The tables give the reader a fair picture of the relative importance of the different items which go into commercial fertilizers. It should be borne in mind however that this does not represent the total fertilizer activity of the country. The growing of nitrogen-fixing plants (legumes) and the use of manure add tremendously to soil fertility, particularly of nitrogen. That production does not enter into commercial columns.

Viewing the commercial fertilizer picture as a whole it may be said that it is becoming more and more of a bona fide chemical industry; uses are increasing, prices are decreasing and the synthetic and chemically modified materials are rapidly overshadowing the older natural materials. In addition there is a definite trend to use more concentrated fertilizers of carefully controlled composition. Agricultural activities are becoming more closely tied to chemical industry.

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SECTION III

FUELS AND THEIR BY-PRODUCTS

The industries considered in this section are based largely on the application of the unit process of pyrolysis—the partial decomposition of organic materials by heat—though the production of straight-run gasoline would not fall under this heading. As the chemical industry has grown up, the by-products have shown a propensity for becoming the tail that wags the dog. This is particularly true of the products of wood distillation industries and of industrial carbon.

CHAPTER 14

THE PETROLEUM INDUSTRY

Gustav Egloff
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INTRODUCTION

During the past thirty years or so, the petroleum industry has become one of the basic industries upon which our present civilization is founded. Through the products which it has made available in vast quantities, rapid transportation has become the rule rather than the exception, and the trend is toward even more rapid transportation than exists today. The application of scientific and engineering principles to the petroleum industry are the basis of the development which has given the United States a fourteen billion dollar industry. During 1940, about 557,904,000 barrels of gasoline were produced from 1,295,059,200 barrels of crude oil (42 gallons = barrel), with another 54,549,600 barrels of gasoline coming from natural and casinghead gases. As a subject for research, crude oil presents complex problems which are economically important as well as interesting. Petroleum is composed essentially of many thousands of hydrocarbons. The problem of separating and identifying these hydrocarbons has not yet been solved, nor has the importance of these compounds to science and technology been fully realized.

The Origin of Petroleum—The origin of petroleum has never been satisfactorily explained, although chemists, physicists, and geologists have proposed a number of theories. There are two classes into which theories fall. The first is the inorganic group, postulating that petroleum was formed from metallic compounds of carbon found in the earth; another theory proposes that hydrocarbons were originally formed during the consolidation of this planet. The second group of theories postulates that petroleum was formed from organic substances present on the earth's surface, but whether they were plant or animal is a question evoking considerable argument. References covering the various theories will be found in the Reading List at the end of this chapter.

Within recent months data indicating that petroleum might have been derived from coral reefs as well as diatoms has added further information to these organic theories.

Whatever its origin, oil has vastly extended our sphere of activity, and petroleum products in addition to motor fuel are singularly important in maintaining commerce at its present level.

Crude Oil Resources—Geologists state that in the United States oil discovery is possible in 1,100,000,000 acres, or 56 per cent of its total land area. The contrast of this huge territory with the 2,000,000 acres now producing oil makes it certain that new fields will be continually discovered and that the oil supply will prove ample for many years to come. The oil resources at the beginning of 1940 were estimated at about 18,483,000,000 barrels.[1] What is true regarding the potential oil production of the United States probably is true in even greater measure for many other countries of the world, where oil exploration has been less thorough than in this country.

As will be shown, from the beginning of production on a significant scale in the year 1859 to the end of 1940, the oil fields of the world produced about 25,365,637,040 barrels of petroleum. It is estimated that at most, 20 per cent of the oil in the ground is brought to the surface. For every barrel of oil produced, four barrels or so remain in the earth. While 25,365,637,040 barrels of oil have come from the wells, 101,462,548,160 barrels or more are still in the oil sands. This oil alone, if it could be recovered by means of flooding, repressuring or mining, would supply the world's needs for over fifty years.

TABLE 1—ESTIMATED YIELD OF VARIOUS PRODUCTS PRODUCED FROM PETROLEUM IN THE UNITED STATES FOR 1940*

Products from Crude Oil	*Thousands of Barrels*
Crude distilled	1,295,059.2
Motor fuel	557,904.0
Straight-run gasoline	264,381.6
Cracked gasoline	293,522.4
Kerosene	72,668.4
Gas oil and distillate fuels	181,947.6
Residual fuel oils	314,601.6
Lubricants	37,054.8
Still gas† (millions cu. ft.)	275,702.4
(bbls.)	72,553.2
Wax (lb.)	510,720.0
Coke (short tons)	1,574,400.0
Asphalt (short tons)	5,548,320.0

* Based on Monthly Petroleum Statement, U. S. Bureau of Mines, No. 204, December 11, 1940.

† Based on 3,800 cu. ft. as equivalent to a barrel.

Since the foundation of the petroleum industry many predictions of oil shortage have been made. But despite the stupendous increase in the use of petroleum during the last two decades, discovery of new fields has never failed to keep pace with the demand. At the present time the world's output of oil is far below the capacity of the wells now producing. Proration and drilling agreements are holding back a veritable flood of crude, which could be produced in amounts far exceeding present requirements. In view of the known crude oil reserves, the vast amount left underground by present production methods, and the undiscovered fields that no doubt exist, an oil shortage, despite the gloomy prophets, is far in the future. It may not be too optimistic to predict, considering past and present experience throughout the world, that crude oil will be our dominant source of gasoline for at least a century to come.

Products from Crude Oil—Petroleum first taken from the ground and not yet refined in any way is called "crude oil." The principal products from crude oil are given in Table 1. With the exception of still gas used in the chemical

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[1] American Petroleum Institute Quarterly, *10,* No. 2, 8 (1940).

industries, these products find utilization in the state in which they come from the refinery.

Development of the Petroleum Industry—In 1940 the world produced over 2,150,679,000 [2] barrels of petroleum. With the 1940 volume of crude oil should be compared the 150,000,000 barrels which was the world's total production in 1900, or the 400,000,000 barrels in 1914.

The United States is by far the largest producer of crude oil. Besides the United States the great producers of crude oil are Russia, Venezuela, Iran, Netherlands East Indies, Rumania, and Mexico. Of the 1940 production the United States produced 1,345,752,800 [2] barrels, or about 61 per cent. The consumption rate for the United States for 1940 was about 592,724,000 barrels of motor fuel from all sources including gasoline from natural gas and benzol from coal tar in the United States to fill the needs of its 32,000,000 automobiles, busses, trucks, tractors and motorcycles. Table 2 shows the petroleum production of the United States and of the world by decades since 1859.

TABLE 2—WORLD'S PRODUCTION OF CRUDE PETROLEUM *

(Thousands of Bbls. of 42 U. S. Gals.)

Year	*World*	*United States*
1859	6	2
1860	509	500
1870	5.799	5,261
1880	30,018	26,286
1890	76,633	45,824
1900	149,137	63.621
1910	327,763	209,557
1920	688,804	472,929
1930	1.411,904	898,011
1940	2,150,679	1,345,752,800
World Total: 1859-1940		25,365,637,040

* Petroleum Facts and Figures, p. 57, authority U. S. Bureau of Mines, American Petroleum Institute (1937).

MOTOR FUEL FROM CRUDE OIL

General—During the past twenty years a tremendous amount of research has been carried out on the art of distilling crude oil. Distillation units with capacities ranging from a few hundred to over sixty-five thousand barrels of crude oil per day have been developed to fractionate the gasoline present with such exactness that little or no further refining is required. The gasoline produced in the earlier days of distilling petroleum was treated with sulfuric acid and caustic soda and then redistilled to a commercial product. Today, acid treatment is no longer necessary, for gasoline derived by distillation of crude requires, in general, no refinement beyond sweetening (the changing of mercaptans to sulfides by means of sodium plumbite or copper salts).

Modern motors operate with much higher compression ratios than formerly, to obtain more power and greater efficiency. Hence, it is highly desirable to have fuels that will not "knock" in the high compression motors.

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[2] Oil and Gas Journal, Dec. 26, 1940, p. 63.

The antiknock value of straight-run (i.e., straight distillation of crude oil) gasoline[8] varies widely; its octane number ranges from approximately 15 to over 70. Very little of the latter is available and averages about 53. The octane rating of a motor fuel is determined in a motor under standardized conditions using as a measure normal heptane which is rated at zero octane number and 2, 2, 4-trimethylpentane ("isooctane") rated at one hundred. The unknown gasoline is tested against known percentages of isooctane in normal heptane and when the two motor fuels match in motor performance, the octane number of the unknown fuel is determined.

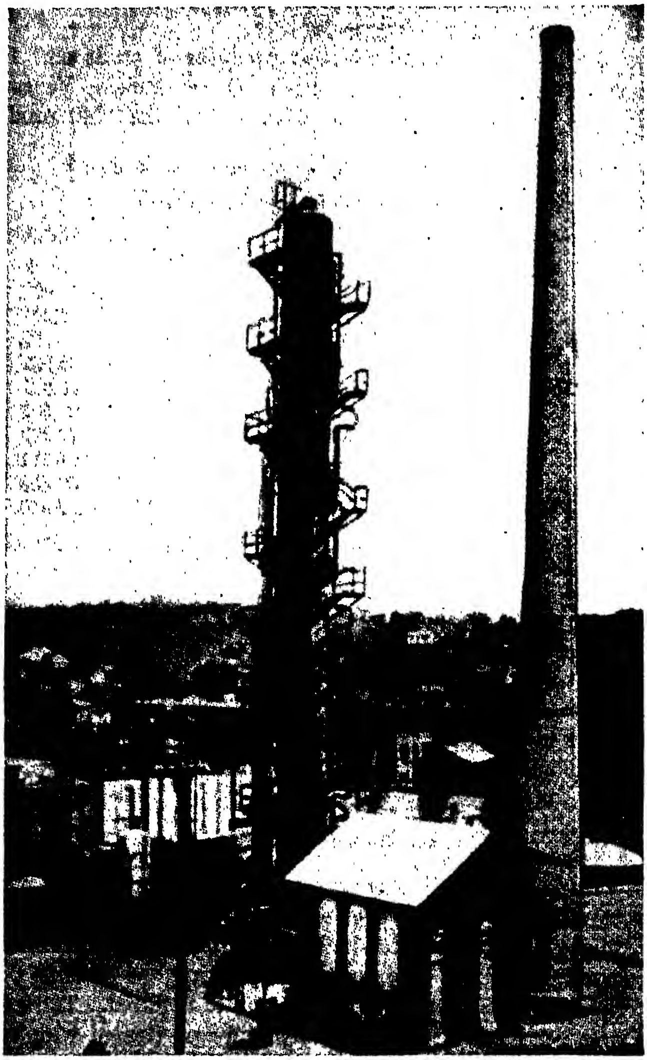

Fig. 1. Crude-oil Distillation Unit in Pennsylvania.

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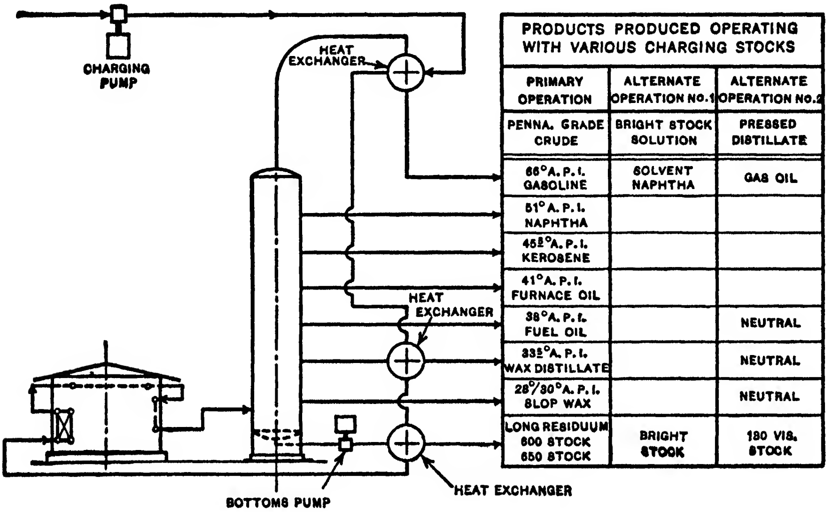
[8] Egloff, G., Hubner, W. H., and Van Arsdell, P. M., Chem. Reviews, *22*, 175 (1938).

The average value of 53 octane for straight-run gasolines is too low for modern high-compression engines and is in part reformed or cracked, i.e., the straight-chain paraffins which have low octane ratings are converted by heat and pressure into olefinic, aromatic, and naphthenic hydrocarbons which have greater antiknock properties.

The cracking of hydrocarbon oils such as gasoline, naphtha, kerosene, gas oil, fuel oil, or crude oil, produces gasolines whose octane numbers range from approximately 60 to over 80 with an average of about 69. The quality of the cracked gasoline depends upon the type of oil processed, the time, temperature, pressure, and principle of operation used.



PRODUCTS PRODUCED OPERATING WITH VARIOUS CHARGING STOCKS		
PRIMARY OPERATION	ALTERNATE OPERATION NO. 1	ALTERNATE OPERATION NO. 2
PENNA. GRADE CRUDE	BRIGHT STOCK SOLUTION	PRESSED DISTILLATE
66° A. P. I. GASOLINE	SOLVENT NAPHTHA	GAS OIL
51° A. P. I. NAPHTHA		
45½° A. P. I. KEROSENE		
41° A. P. I. FURNACE OIL		
38° A. P. I. FUEL OIL		NEUTRAL
33½° A. P. I. WAX DISTILLATE		NEUTRAL
28°/30° A. P. I. SLOP WAX		NEUTRAL
LONG RESIDUUM 600 STOCK 650 STOCK	BRIGHT STOCK	180 VIS. STOCK

FIG. 2. Flow Sheet of Crude-oil Distillation Unit.

The production from crude oil of cracked gasoline (1940) represents 52.6 per cent of the total, while that of straight-run gasoline is 47.4 per cent.

Straight-Run Gasoline from Distillation of Crude Oil—The distillation of crude oil at atmospheric pressure may be carried out in a unit such as shown in Figures 1 and 2. Pennsylvania crude is used as an illustration. The crude oil, before passing through the heating coil of the furnace, is pumped through a series of heat exchangers counterflow to the hot vapors and liquids leaving the bubble tower fractionator.[4] The temperature of the oil is about 800° F. as it leaves the heating coil and flows into the fractionating column. The products derived from this primary distillation of Pennsylvania crude oil (42-43° A.P.I. gravity) are gasoline, naphtha, kerosene, furnace oil, fuel oil, wax distillate, and heavy lubricating oil stock and bottoms.

THERMAL CRACKING

Straight-run Gasolines and Naphthas—The outstanding development in the early days of gasoline manufacture was the introduction of the process of

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[4] See Chapter 2.

cracking. This is essentially high temperature decomposition, which in the language of the organic chemist is usually called pyrolysis.[4] When organic compounds of high molecular weight are subjected to high temperature and pressure, new materials are formed, usually of lower molecular weight. By proper control of the cracking process in the petroleum industry it is possible to get as much as three quarters of a barrel of gasoline from a barrel of crude oil, whereas, the yield from straight-run distillation is only about 20 to 25 per cent. Hence, it is seen that the introduction of cracking tremendously increased the potential yield of gasoline from our crude oil. As was reported above, the amount of cracked gasoline produced in this country at the present time is over half of the total.

TABLE 3—PROPERTIES OF PRODUCTS FROM PRIMARY DISTILLATION OF PENNSYLVANIA 42-43° A.P.I. GRAVITY CRUDE OIL

Properties	*Gasoline* *		*Naphtha*	*Kerosene*	*Furnace Oil* †	*Fuel Oil* †	*Bottoms, 665 Fire Stock* ‡
	Light	*Heavy*					
Gravity, ° A.P.I.	80.0	64.0	51.1	45.7	40.0	38.0	25.0
Distillation characteristics:							
Initial boiling point, ° F.	70	120	305	400	340	540	...
10 per cent	100	175	330	413	491	583	...
20 per cent	115	196	334	418	512	589	...
50 per cent	158	237	344	433	528	601	...
90 per cent	258	293	375	468	550	622	...
End point, ° F.	270	320	419	498	574	635	...
Flash point, ° F.	...	...	...	185	...	...	590
Fire point, ° F.	...	...	...	205	...	...	665
Flash point P.M., ° F.							590
Viscosity, S.U. at 210° F.							202

* The light gasoline shown, having an A.P.I. gravity of 80 and representing 3.5 per cent of the crude or 13.8 per cent of the total gasoline, was preflashed and not fractionated.

† Furnace oil and fuel oil may be varied as the market demands.

‡ While the unit was designed for taking off a slop wax, the fraction usually is sufficiently sharp to eliminate the necessity of this cut.

Besides producing far more gasoline per barrel of crude oil, cracking also produces a gasoline of considerably better quality for use in gasoline motors. This comes about because the cracking process tends to produce branched-chain paraffins or ring compounds which have higher antiknock properties than the straight-run gasolines.

When the heavier or high molecular weight materials of the crude oil are subjected to sufficient heat and pressure to break them down into smaller molecules, the process is ordinarily called cracking, but when a gasoline is put through the same operation, conditions can be controlled so that there is not a great deal of breakdown of the molecules but there is a molecular rearrangement or "reforming" to give more of the branched-chain paraffins which have better antiknock characteristics. Hence, when a gasoline fraction is subjected to this pyrolysis it is called "reforming."[5]

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[5] See Chapter 3.

In the processes of cracking or reforming, it is not possible to predict what the products will be. Experimentation in this field relies entirely upon empiricism and experience. In general, however, it may be said that the products which are formed from a given raw material are dependent in various ways upon the temperature, the pressure, the length of time, and the amount and kind of catalyst which may be used.

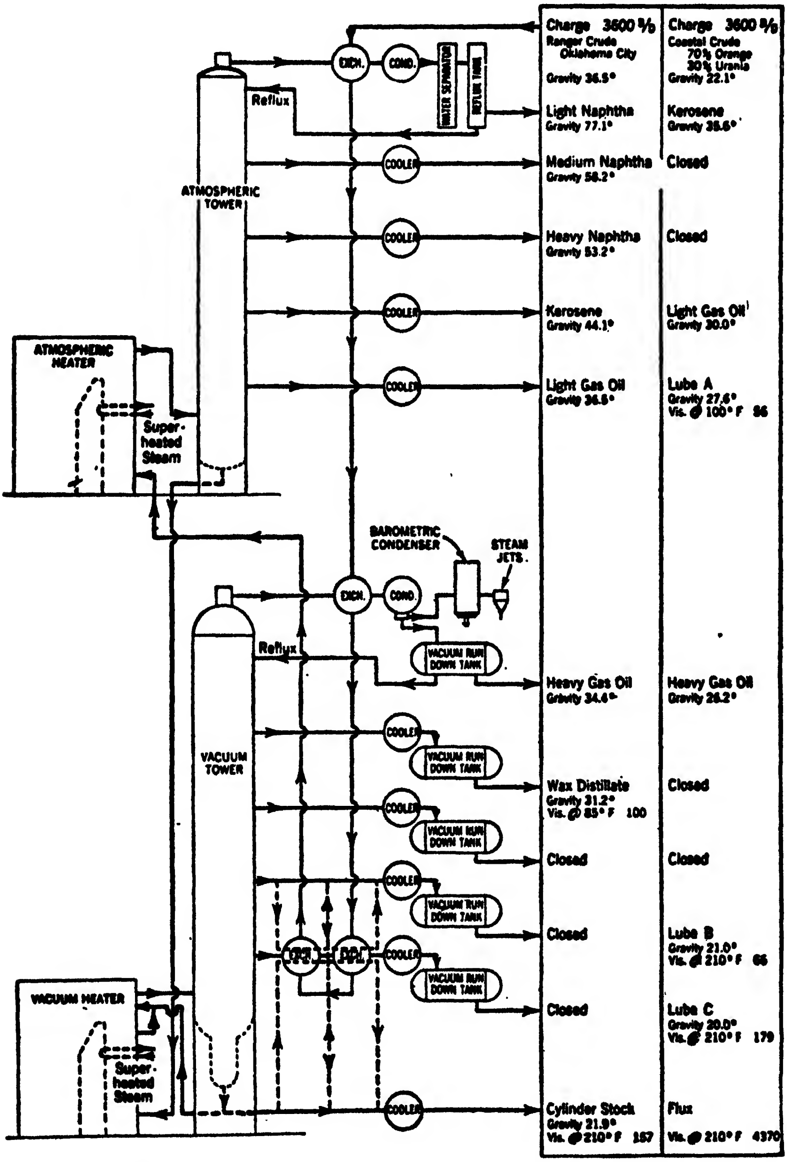

FIG. 3. Two-stage Atmospheric and Vacuum Crude Distillation Unit. (Courtesy Foster Wheeler Corp.)

Table 3 shows the distillation products from a 42-43° A.P.I. gravity Pennsylvania crude oil.

A distillation unit combining vacuum and atmospheric pressure is shown in Figure 3. The products shown are from Ranger crude from Oklahoma City

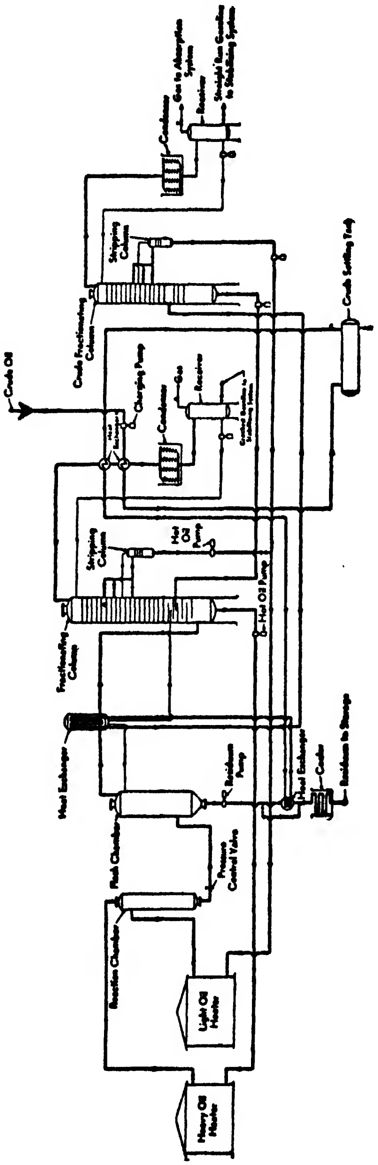

FIG. 4. Flow Sheet of a Topping and Cracking Unit.

Due to the development of high-compression motors, straight-run gasoline is no longer suitable as a fuel. It is necessary to convert the straight-run distillation product to hydrocarbons which possess greater antiknock properties. The branched-chain paraffins are the most desirable type at this time due to their slow burning characteristics compared to the straight-run gasolines; however, olefins, naphthenes, and aromatics are also suitable. To convert the knocking gasolines into non-knocking ones, temperatures of the order of 1025° F. and pressures above 750 lbs. per square inch are used. Gasoline reforming units for the production of high-octane motor fuel consist of a heating coil and fractionating tower, or they may be part of a topping, reforming, and heavy oil cracking installation as shown in Figures 4 and 5. It is estimated that 30 per cent of the 264,381,600 barrels of straight-run gasoline produced during 1940 was reformed into gasoline of higher octane number. The quantity of reformed gasoline increases yearly in order to meet the demand for high-octane gasoline.

Octane ratings and laboratory inspection data[6] for reformed and cracked gasolines, as produced from various crudes, are given in Tables 4, 5 and 6.

As noted in Table 4, the reforming stocks varied from straight-run naphtha to light gasoline. Yields of reformed gasoline with octane ratings of 57 to 80 ranged from 38 per cent to more than 88 per cent, depending upon the cracking plant operating conditions and the type of stock used.

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[6] Egloff, G., Hubner, W. H., and Van Arsdell, P. M., Chem. Reviews, *22*, 175 (1938).

Heavy Oils to Gasoline—The modern refining of crude oil, when only gasoline is the desired end-product, takes place in combination topping and cracking units. (A topping unit distills the gasoline from the crude oil. The cracking unit produces gasoline from the crudes and topped crudes by means of heat and pressure.) As noted in Tables 5 and 6, in some cases the whole crude was subjected to cracking conditions of heat and pressure to produce the cracked fuel. In other cases either the topped or reduced crude was utilized. The yields of cracked gasoline, based upon the charge of crude oil ranged from 44 per cent to over 63 per cent, with ratings from 68 to 77 octane number. It should be mentioned, however, that both the yield and the quality of the gasoline produced are dependent upon the cracking stock and upon such operating conditions as time, temperature, and pressure.

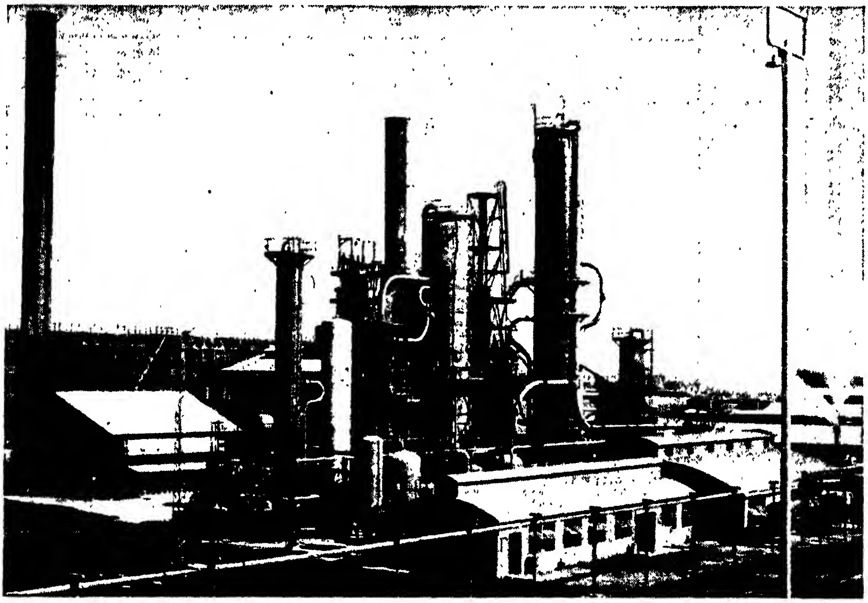

FIG. 5. Topping and Cracking California Crude Oil Unit.

A flow chart of a topping and cracking unit is shown in Figure 4.

The cracking section is based upon the selective principle, which uses two or more heating coils in order that each fraction of the oil may be converted under its best time, temperature, and pressure conditions.

Separating Impurities—The crude oil charged to the unit usually contains water as an emulsion, together with dissolved salts, which it is desirable to remove before processing in the unit. To accomplish this, the crude oil is pumped through a heat exchanger under a pressure of approximately 165 lb. per square inch, where the temperature of the oil is raised to 225° F. It is then passed to a settling chamber. Under these conditions of temperature and pressure the viscosity of the crude oil is reduced, but vaporization of the water is prevented. As a result, the salt water drops out and is removed from the bottom of the settler.

TABLE 4—OCTANE RATINGS AND INSPECTION DATA FOR REFORMED STRAIGHT-RUN GASOLINES AND NAPHTHA FROM VARIOUS CRUDE OILS

Crude Oil-producing Fields and Districts	*Appalachian-Pennsylvania*			*Mt. Pleasant, Michigan*	*Mid-Continent*		*East-West Texas*						*West Texas*			*Rocky Mountain: Montana*	*California*	
Type of reforming stock.......	Light gasoline	Gasoline	Naphtha	Gasoline	Gasoline	Naphtha	Gasoline						Gasoline	Naphtha		Gasoline	Light naphtha	Heavy naphtha
Charging stock:																		
Gravity, °A.P.I.	64.4	58.1	49.8	61.7	59.8	53.6	58.8			Same			58.1	51.5		59.8	46.6	42.4
Sulfur, per cent...........	......	......	......	0.04	......	......	0.14			Same			0.18	0.19		0.11	0.10	0.09
Octane No., C.F.R. motor method.............	49	38	27	20	42	34	54			Same			60	50		51	50	48
Distillation characteristics:																		
Initial boiling point, °F....	117	152	272	152	115	222	99			Same			95	220		126	303	299
10 per cent............	169	215	315	190	177	263	168			Same			160	261		186	311	325
50 per cent............	192	280	329	278	277	309	262			Same			374	312		212	320	361
90 per cent............	301	354	446	360	347	353	360			Same			364	370		340	340	400
End point, °F...........	354	396	479	389	383	385	406			Same			392	410		381	364	427
Operating conditions:																		
Pressure, lb. per square inch	750	500	478	1000	500	500	750	752	750	745	750	750	750	750	750	500	750	750
Furnace discharge, °F.......	975	975	975	985	1000	1000	945	960	975	994	995	995	950	950	950	965	975	970
Reaction chamber, °F.......	925	926	924	935	950	952	899	909	925	993	995	993	896	898	899	915	925	922
Feed rate, gallons per hour..	1.97	0.76	1.04	1.98	1.91	2.03	2.01	1.94	1.98	3.93	3.02	2.06	3.20	2.13	1.58	1.95	1.37	2.02
Cracking results:																		
Gasoline:																		
Yield, per cent of charge..	72.2	66.5	64.0	65.5	74.7	74.3	88.7	82.7	76.0	62.8	48.9	37.9	88.1	81.1	77.4	79.5	69.2	70.5
Gravity, °A.P.I.	63.5	57.3	54.5	61.0	59.1	55.5	58.8	58.7	58.2	52.2	49.8	45.7	59.4	54.5	54.2	60.7	48.3	47.5
Octane No., C.F.R. motor method...........	70	74	74	67	70	70	68	71	72	76	78	80	72	73	75	72	77	77
Distillation characteristics:																		
Initial boiling point, °F..	99	84	88	94	89	91	101	96	96	102	100	106	96	91	100	96	93	88
10 per cent...........	148	154	145	142	146	164	150	146	146	154	158	158	148	171	168	146	179	178
20 per cent...........	172	188	192	193	180	204	179	176	174	186	186	184	178	214	203	176	236	236
50 per cent...........	229	252	289	235	259	280	245	242	238	254	244	234	253	280	277	243	296	316
90 per cent...........	320	384	397	360	356	358	364	372	354	397	362	359	366	378	368	336	350	380
End point, °F..........	363	404	410	396	379	382	403	411	396	436	416	429	400	403	389	386	381	409
Residuum:																		
Yield, per cent of charge...	2.5	4.6	7.6	4.3	1.3	2.5	0.0	0.6	3.5	1.1	5.3	5.7	2.1	5.7	4.8	3.8	8.2	12.8
Gravity, °A.P.I..........	15.0	2.9	17.2	8.5	−0.7	−4.5	......	20.8	16.1	7.1	2.8	0.3	12.9	11.7	12.3	14.6	9.1	17.7
Gasoline content, per cent.	3.5	......	0.0	0.5	......	......	......	5.0	2.0	3.0	1.8	2.0	3.5	4.0	3.0	3.0	3.0	2.0
Loss:																		
Liquid volume, per cent...	25.3	28.9	28.4	30.2	24.0	23.2	11.3	16.7	20.5	36.1	45.8	56.4	9.8	13.2	17.8	16.7	22.6	16.7
Gas, cu. ft. per barrel of charge	645	946	919	789	611	762	380	499	640	1125	1430	1780	369	535	639	778	695	735

TABLE 5—OCTANE RATINGS AND INSPECTION DATA FOR CRACKED GASOLINES FROM VARIOUS CHARGING STOCKS

Stock	*Pennsylvania Kerosene Distillate*	*East Texas*		*West Texas Topped Crude*	*Mid-continent Gas Oil*	*Mid-continent Topped Crude*	*California (Southern) Fuel Oil*
		Crude	*Topped Crude*				
Charging stock analysis:							
Gravity, °A.P.I.	45.0	38.6	29.7	20.9	38.5	26.9	18.1
A.S.T.M. distillation:							
I.B.P. °F.	322	114	245	466	440	420	446
Per cent over at 437° F.	44.0	39.0	19.0	0.0	0.0	2.2	....
Per cent over at 572° F.	92.0	53.0	41.0	17.5	93.5	26.0	14.5
Per cent B.S.&W. (benzol centrifuge)	0.0	Trace	0.7	0.2	Trace	0.8	0.01
Pressures—lbs. per sq. in.:							
Reaction chamber	360	350	300	200	350	250	200
Flash chamber	50	50	50	50	50	50	50
Temperatures, °F.:							
Transfer from tubes to reaction chamber	938	950	950	925	950	950	925
Yields, per cent based on charging stock:							
Gasoline	69.8	70.6	63.3	47.6	72.8	62.2	40.2
Residuum	7.0	18.6	25.7	44.9	11.9	28.8	52.6
Coke, gas and unacc. loss	23.2	10.6	11.0	7.5	15.3	9.0	7.2
Gas, cu. ft. per bbl. of charge	650	397	543	473	634	481	412
Analysis of products:							
Gasoline:							
Gravity, °A.P.I.	63.6	59.8	56.7	60.0	61.0	56.4	58.0
A.S.T.M. distillation:							
I.B.P. °F.	85	102	98	88	84	90	88
20 per cent	171	180	202	173	170	185	174
50 per cent	248	259	290	248	251	292	262
90 per cent	336	381	384	340	357	416	380
End point	355	404	399	375	387	425	403
Octane No. (A.S.T.M.) motor method	71	68	68	72	74	70	68
Residuum							
Gravity, °A.P.I.	7.4	4.3	3.5	6.2	5.5	4.8	7.9
Per cent B.S.&W.	0.5	0.1	0.6	0.5	0.1	0.6	0.2
Visc. S. F. at 122° F.	....	311	347	105	18	318	250

TABLE 6—OCTANE RATINGS AND INSPECTION DATA FOR CRACKED GASOLINES FROM VARIOUS CRUDE OILS

Crude Oil-producing Fields and Districts	*Appalachian*	*Michigan, Indiana, Illinois*	*Mid-Continent*					*Gulf Coast*			*Rocky Mountain*		*California*	
	Corning, Ohio	*Mt. Pleasant, Michigan*	*Kansas*	*East Texas*	*West Texas*	*Smackover, Arkansas*	*Rodessa, Louisiana*	*White Castle, Louisiana*	*Placedo, Texas*	*Flour Bluff, Texas*	*Rex Lake, Wyoming*	*Pondera, Montana*	*Signal Hill*	*Los Alamos*
Type of cracking stock	Reduced crude	Topped crude	Topped crude	Reduced crude	Heavy naphtha and topped crude	Topped crude	Topped crude	Whole crude	Whole crude	Reduced crude	Topped crude	Topped crude	Topped crude	Whole crude
Cracking stock:														
Yield, per cent of crude	68.0	65.7	......	52.9	90.0	89.8	63.2	100	100	24.1	70.4	61.9	83.2	100
Gravity, °A.P.I.	28.4	31.0	25.5	26.6	27.4	17.9	35.0	24.0	24.4	27.8	27.4	20.1	20.6	14.1
Cracked gasoline:														
Yield, per cent of cracking stock	61.0	63.5	57.9	54.5	61.0	43.7	61.7	59.0	58.6	57.4	59.8	51.4	48.2	44.1
Gravity, °A.P.I.	59.4	62.3	60.4	59.9	56.0	57.5	63.7	52.7	51.3	59.5	59.0	58.9	56.9	54.0
Octane No., C.F.R. motor method	Approx. 68	64	71	68	69	72	70	Approx. 80	77	70	70	68	71	72
Sulfur, per cent	0.08	0.05	0.06	0.07	0.23	0.26	0 05	0.06	0.06	0.03	0.09	0.29	0.55	1.84
Distillation characteristics:														
Initial boiling point, °F	90	92	88	90	99	91	96	104	95	97	96	90	99	98
5 per cent	126	125	124	112	132	126	116	132	134	122	123	123	127	133
10 per cent	146	143	136	124	157	140	130	153	154	137	138	144	145	155
20 per cent	182	172	164	156	198	....	157	190	192	....	162	180	177	193
50 per cent	268	246	236	244	284	262	226	280	277	243	256	270	364	276
90 per cent	390	342	346	364	384	364	334	376	372	342	355	370	357	366
End point, °F	404	374	406	404	394	397	393	399	401	412	395	397	396	400
Per cent over	98.0	98.0	98.0	97.0	97.0	97.5	97.5	97.0	95.0	98.0	97.0	95.0	98.0	96.5
Per cent bottoms	1.0	1.0	1.0	1.0	1.5	1.0	1.0	1.5	1.0	1.0	1.0	1.0	1.0	1.0
Per cent loss	1.0	1.0	1.0	2.0	1.5	1.5	1.5	1.5	4.0	1.0	2.0	4.0	1.0	2.5

Distillation—The crude oil then flows from the top of the settling tank through a series of heat exchangers to increase the temperature to approximately 550° F. The preheated oil is passed to the crude oil fractionating column, where the gasoline is distilled and then condensed, flowing to a storage tank. In the unit shown in Figure 4, the fractionating column for this service is 11 ft. in diameter and 49 ft. high. The topped crude from the bottom of the fractionating column is pumped directly to the bubble tower of the cracking unit.

Cracking—The cracking unit fractionating column is 11 ft. in diameter and 74.5 ft. high. The topped crude passing down through this column contacts the hot ascending vapors and a partial fractionation takes place.[7] The vapors passing up the column are separated as a liquid sidecut and an overhead consisting of gasoline and gas. The liquid sidecut, called light oil, is pumped from one of the bubble decks to the light-oil furnace tubes and heated to a temperature of approximately 960° F. The gasoline vapors and gas pass from the top of the fractionating column through a cooling coil to a receiver, where a separation of gasoline and gas is made. The unconverted oil from the bottom of the fractionating column, referred to as heavy combined feed and consisting of the heavy ends of both the charge and the vapors condensed in the tower, is pumped through the heavy-oil furnace tubes, where the temperature is raised to approximately 925° F.

The ratings of the light- and heavy-oil heaters are 53 and 61 million B.t.u. per hour absorbed by the oil. The outlet pressures of the two heaters are 300 and 280 lb. per square inch, respectively. The heated hydrocarbons from both these heaters pass to the top of the reaction chamber, which is 7 ft. in diameter and 50 ft. high and is maintained at a pressure of 275 lb.

The hydrocarbon mixture from the bottom of the reaction chamber passes to the primary flash chamber, which is 11 ft in diameter and 40 ft. high. The flash chamber and subsequent equipment through the condenser to the receiver are maintained at a pressure of approximately 100 lb. per square inch. The material entering the flash chamber is separated into bottoms of cracked unflashed residue and overhead vapors of gas, gasoline, and recycle stock. The vapors from the top of the flash chamber pass through a heat exchanger into the fractionating column, where they contact the topped crude oil as previously described. The unflashed residue passes to a secondary flash chamber, which is 6 ft. in diameter and 28.5 ft. high, maintained at about 20 lb. pressure. The material entering this chamber separates into low-gravity cracked residuum bottoms and overhead vapors which are returned to the fractionating column. The residuum is blended with part of the sidecut of the column to produce a blended residue meeting fuel-oil specifications.

The vapors from the top of the fractionating column, at a temperature of 380° F., pass through heat exchangers and a condenser into a receiver, where a separation of the gas and cracked gasoline is made. The cracked gasoline has the required end point and flows to a stabilizer to produce the required vapor pressure, which normally varies from 8 to 12 lb. per square inch at 100° F. depending upon the season of the year. (A stabilizer is essentially a distillation unit in which small amounts of the more volatile constituents are removed, to reduce the vapor pressure of the gasoline to the desired point.) The cracked

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[7] **For a discussion of the principles of fractionation, see Chapter 2.**

gasoline may be water-washed, caustic soda-treated, or sweetened and then fortified against deterioration by antioxidants. It may be colored by a dye, and as such is suitable for marketing.

A typical commercial run of thirty days in the described plant, processing 373,650 barrels of California crude oil at the rate of 12,500 barrels per day, produced an average of 64.03 per cent motor fuel, 28.86 per cent 5.1° A.P.I. gravity cracked fuel oil, and 7.11 per cent gas and loss.

TABLE 7—SUMMARY OF VOLUMES AND PERCENTAGES OF PRODUCTS PRODUCED WHEN TOPPING AND CRACKING CALIFORNIA CRUDE OIL

Operation and Products	*Total No. of Bbls.*	*Bbls. per Day*	*Per Cent of Charge*
Topping operation:			
Crude oil	373,650	12,455	100.00
Products:			
Straight-run gasoline	119,670	3,989	32.03
Topped crude	250,200	8,340	66.96
Gas and loss	3.780	126	1.01
Totals	373,650	12,455	100.00
Cracking operation:			
Topped crude	250,200	8,340	100.00
Products:			
Cracked gasoline	119,580	3,986	47.79
Cracked residuum	107,820	3,594	43.09
Gas and loss	22,800	760	9.12
Totals	250,200	8,340	100.00
Combination topping and cracking operation:			
Products processed:			
Crude oil	373,650	12,455	100.00
Products:			
Straight-run gasoline	119,670	3,989	32.03
Cracked gasoline	119,580	3,986	32.00
Total gasoline	239,250	7,975	64.03
Cracked residuum	107,820	3,594	28.86
Gas and loss	26,580	886	7.11
Totals	373,650	12,455	100.00

Time on stream = 30 days; total gas produced = 122,400,000 cu. ft.

A summary of the operating conditions used and of the volumes and properties of the products produced is given in Tables 7 and 8.

Catalytic Cracking—Catalytic cracking is a comparatively new process used to increase the octane rating and yields of gasolines produced from crude oil. Catalytic cracking of crude oil has been developed in order that higher octane fuels may be produced than are possible with thermal processes. The thermal processes are limited because they must go to extremely high temperatures and pressures to produce comparable results. A mid-continent gas oil on a U.O.P. (Universal Oil Products) catalytic cracking test gave an overall yield of 85 per cent of 81 octane gasoline on a recycle basis. When the cracked gases produced in this process are selectively polymerized and hydrogenated,[8] a 12 per cent yield of 96 octane gasoline is obtained which is suitable for airplane

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[8] See p. 560.

use. The 96 octane gasoline consists of branched paraffins, predominantly isooctanes, that are particularly desirable because of high antiknock value. In addition to the yield of branched paraffins, 73 per cent of 81 octane gasoline is derived from mid-continent gas oil which may be used as premium grade motor fuel.

TABLE 8—ANALYSES OF STRAIGHT-RUN AND CRACKED GASOLINE PRODUCED WHEN TOPPING AND CRACKING CALIFORNIA CRUDE OIL

Properties	*Crude Oil*	*Straight-Run Gasoline*	*Cracked Gasoline*	*Blended Residue*
Gravity, °A.P.I.	30.5	52.1	59.6	5.1
Distillation characteristics:				
Initial boiling point, ° F.	156	126	102	...
10 per cent	277	199	142	...
30 per cent	441	248	184	...
50 per cent	583	287	241	...
90 per cent	687	389	344	...
End point, °F.	...	425	383	...
Per cent distilled at 300° F.	12	...	...	...
Per cent distilled at 400° F.	26	...	...	...
Octane No., C.F.R. motor method	...	56	71	...
Reid vapor pressure, lb. per square inch at 100° F.	...	5.0	9.3	...
Sulfur, per cent	0.65	0.06	0.37	...
Color	...	25	...	...
Viscosity, S.F. at 122° F.	...	...	...	240
Flash point, P.M., ° F.	...	...	...	194
B. S. & W., per cent	...	...	...	0.1

An analysis of the cracked gases produced in the U.O.P. catalytic cracking process is shown in Table 9.

TABLE 9—CRACKED GAS ANALYSIS

	Per Cent
H_2	15.9
CH_4	18.5
C_2H_4	4.8
C_2H_6	5.2
C_3H_6	21.5
C_3H_8	5.1
C_4H_8 (iso)	8.8
C_4H_8 (*n*)	12.3
C_4H_{10}	5.0
O_2	0.3
CO	0.6
N_2	2.0

Operation of the Unit. The catalytic cracking plant consists of heater and catalyst chambers and is controlled automatically. The flow of stock from the furnace goes to alternate reactors in order that reactivation of the catalyst may take place. The duration of the cycle is about 40 minutes.

The catalytic cracking unit operating at 15 lbs. gauge pressure with banks of catalyst reactors is charged with a catalyst of the alumina silica type. Automatic controls alternate the flow of heated oil first through one-half the catalyst reactors and then through the second half while the first set is regenerated with air. The catalyst is quite rugged. Carbonaceous material collecting on the catalyst causes the activity to diminish, and in order to reactivate, oxidation is brought about under carefully controlled temperatures and amounts of oxygen.

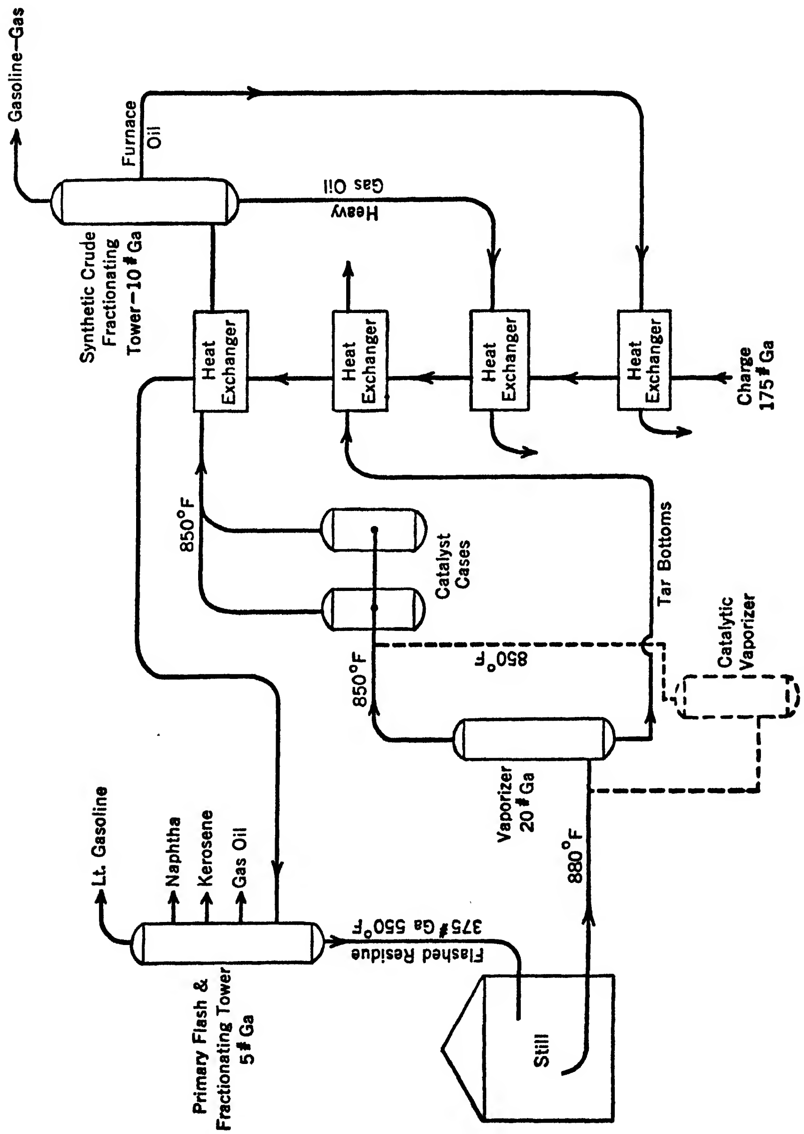

Fig. 6. Flow Sheet of the Houdry Process.

Houdry Process. The Houdry process for the catalytic cracking of crude oils gives a 45 per cent yield of gasoline for one pass through the unit. Activated aluminum hydrosilicate is used to catalyze this reaction and two catalyst chambers are used in order that proper reactivation may occur and permit continuous operation of the process. A flow chart of the process is shown in Figure 6, giving the general steps used in processing a crude oil running to fuel oil, with one pass through the catalyst and with the removal of straight-run products optional. The dotted line indicates the flow if desired to run to "no residuum."

As shown in the flow diagram, crude oil is pumped through heat exchangers, where it is preheated by the products from the catalytic cases, thence to a primary flash fractionating tower, the desired straight-run products being fractionated and removed. The residue from the flash tower is pumped through a still, heated to approximately 880° F.—depending on stock—thence into a vaporizer. Tar bottoms are removed as a liquid, and the vaporized fractions of the charge pass to the catalyst chambers. From the catalyst chambers the vapors pass through the crude-oil exchanger into the final fractionating tower. Gasoline, furnace oil, and heavy gas oil are separated—the latter two being combined, if desired, for recharge to catalytic- or thermal-cracking operations. If gas oil is charged, the flash tower and the vaporizer are eliminated, the charge being pumped through exchangers to the still, and thence directly to the catalyst. If a residue is to be charged, the primary flash fractionating tower is eliminated—the charge passing directly to the still, and thence to the vaporizer for tar separation. To eliminate fuel oil production, the charge from the still is charged to a vaporizer—wherein, through a special catalytic mass, the entire charge is vaporized and passed to the catalyst. In special cases it is advisable to charge the entire crude to the catalyst without removal of straight-run products. The flow arrangement for this operation is the same as described for "residues."

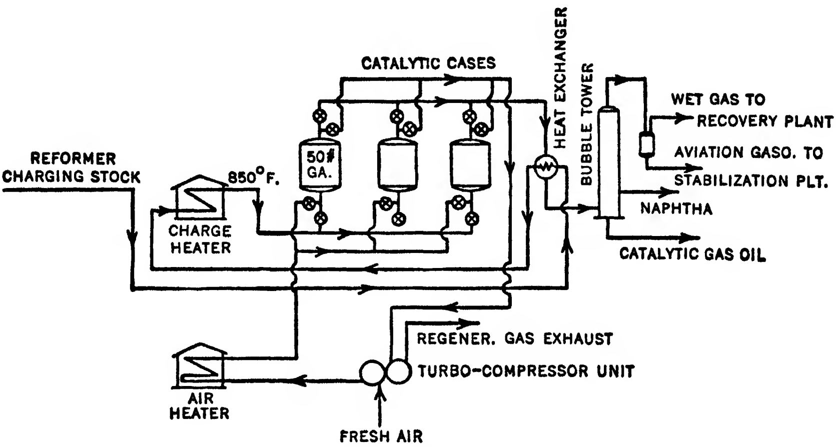

FIG. 7. General Flow Diagram for Processing Reformed Stock.

Tables 10 and 11 show the yields and characteristics of the products obtained from the catalytic cracking of crude oil and gas oil.

Catalytic Reforming.[9] Reforming gasolines by the Houdry process yields aviation base gasolines of high octane rating. These gasolines are chemically stable and have high susceptibility to addition agents and blending materials. The flow diagram Figure 7 shows the scheme of processing the reformed charging

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[9] See p. 534.

TABLE 10—YIELDS AND PRODUCT CHARACTERISTICS BY RUNNING CRUDES AND RESIDUUMS TO FUELS—ONE PASS

Type Crude	*East Texas*		*Grade "B" Coastal*		*36-Deg.-A.P.I. Mid Continent*		*West Texas*		*Mt. Pleasant*		*Lagunillas*
	Topped of Straight-run Naphtha	*Topped of Naphtha, Kerosene, and Furnace Oil*	*Topped of Naphtha*	*Running Entire Crude*	*Topped of Naphtha*	*Topped of Naphtha and Kerosene*	*Topped of Naphtha*	*Topped of Naphtha and Gas Oil*	*Topped of Naphtha*	*Topped of Naphtha, Kerosene, and Gas Oil*	*Running Entire Crude*
Charge to plant, per cent crude	58.5	38.0	75.6	100.0	66.7	52.4	68.5	35.0	62.0	43.3	100
Sulfur content of charge to plant, per cent	0.45	0.55	0.28	0.17	0.48	0.61	1.9	2.20	0.65	0.66	2.14
Tar:											
Per cent volume of crude	8.0	8.0	6.0	6.0	8.4	8.4	8.7	8.50	2.7	8.3	35.4
A.P.I. gravity, deg.	12.6	12.6	12.8	12.8	13.3	13.3	7.4	8.5	11.0	14.8	4.2
Charge to catalyst:											
Per cent volume of crude	50.5	30.0	69.6	94.0	58.3	44.0	59.8	26.5	59.3	35.0	64.6
A.P.I. gravity, deg.	29.0	23.9	26.8	31.9	30.0	27.7	27.0	20.5	31.5	27.2	25.2
Initial boiling point, deg. F.	452	508	415	120	420	538	430	605	415	574	182
50-per-cent point, deg. F.	690	740	615	560	650	711	685	717	625	712	672
End point, deg. F.	760+	760+	760+	760+	760+	760+	760+	760+	760+	760+	760+
Dry gas, per cent by weight of charge to catalyst	4.5	5.1	7.0	3.9	4.0	5.4	5.7	3.1	5.6	5.3	3.8
Catalyst deposit, per cent by weight of charge to catalyst	5.3	5.4	4.4	3.4	3.9	3.5	5.3	4.5	5.2	4.9	4.5
Gasoline:											
Per cent by volume of charge to catalyst	44.0	42.6	47.2	60.6	41.9	44.1	45.3	39.1	40.2	47.0	44.5
A.P.I. gravity, deg.	64.6	61.7	58.9	57.0	63.5	60.8	62.4	59.8	61.1	63.1	61.5
50-per-cent point, deg. F.	229	250	264	270	251	247	258	253	242	232	254
90-per-cent point, deg. F.	351	372	390	384	392	366	384	348	385	363	356
End point, deg. F.	401	412	429	425	440	413	424	397	424	416	396
Reid vapor pressure, lb. per sq. in.	11.0	10.0	11.0	11.0	11.0	11.0	11.0	10.0	11.0	11.0	10.0
Sulfur content, per cent	0.03	0.05	0.02	0.02	0.06	0.06	0.14	0.23	0.03	0.04	0.13
Copper-dish gum, mg. per 100 ml.	7	4	5	4	6	19	34	22	6	8	10
Octane No., A.S.T.M. motor method	78.8	78.8	78.6	73.8	76.8	78.4	77.6	81.0	77.0	79.4	77.7
Catalytic gas oil:											
Per cent by volume of charge to catalyst	54.4	56.4	49.2	38.8	57.7	54.9	51.7	61.2	55.7	51.3	54.7
A.P.I. gravity, deg.	29.5	26.9	26.0	26.3	30.8	28.6	26.2	20.2	33.1	26.5	22.7
Initial boiling point, deg. F.	404	458	403	405	447	436	438	440	415	462	406
50-per-cent point, deg. F.	554	566	517	517	546	579	534	664	531	588	534
Pour point, deg. F.	+45	+50	−10	−10	+30	+45	+10	+45	+10	+35	−(−60)
Viscosity (Saybolt Universal) at 100 deg. F., sec.	39	43	36	36	39	42	38	58	36	43	39
Sulfur content, per cent	0.24	0.31	0.11	0.11	0.20	0.21	1.06	1.04	0.14	0.29	1.17
Aniline point, deg. F.	134	142	125	127	140	140	134	130	135	124	95.7
Liquid recovery, per cent by volume of charge to catalyst	98.4	99.0	96.4	99.4	99.6	99.0	97.0	100.3	95.9	98.3	99.2
32-deg.-A.P.I.-gravity furnace oil in catalytic gas oil, per cent	42.4	......	......	......	......	......	......	9.8	100	13.3	35.6

TABLE 11—YIELD AND PRODUCT CHARACTERISTICS BY RUNNING GAS OILS—ONE PASS

Type Crude	*Mid Continent Gas Oil*	*West Texas—New Mexico Gas Oil*	*East Texas Gas Oil*	*Coastal Gas Oil*
Sulfur content of charge to plant, per cent	0.22	0.81	0.16	0.04
Charge to catalyst:				
A.P.I. gravity, deg.	37.8	30.4	34.5	30.0
Initial boiling point, deg. F.	416	440	420	406
50-per-cent point, deg. F.	536	554	574	494
End point, deg. F.	656	683	750	602
Dry gas, per cent by weight of charge to catalyst	4.3	5.2	6.1	4.9
Catalyst deposit, per cent by weight of charge to catalyst	3.3	4.0	3.2	1.0
Gasoline:				
Per cent by volume of charge to catalyst	44.7	41.0	44.4	50.3
A.P.I. gravity, deg.	64.4	60.8	62.7	56.8
50-per-cent point, deg. F.	233	230	242	260
90-per-cent point, deg. F.	346	354	362	382
End point, deg. F.	398	404	402	410
Reid vapor pressure, lb. per sq. in.	13.0	10.0	11.0	11.0
Sulfur content, per cent	0.02	0.07	0.02	0.01
Copper-dish gum, mg. per 100 ml.	3	9	4	4
Octane No., A.S.T.M. motor method	79.2	79.3	77.0	80.8
Catalytic gas oil:				
Per cent by volume of charge to catalyst	53.0	55.3	51.9	49.9
A.P.I. gravity, deg.	35.2	27.4	31.0	26.6
Initial boiling point, deg. F.	409	419	468	414
50-per-cent point, deg. F.	510	516	550	480
Pour point, deg. F.	+5	−(−60)	+15	−(−60)
Viscosity (Saybolt Universal) at 100 deg. F., sec.	36	37	36	34
Sulfur content, per cent	0.07	0.80	0.10	0.10
Aniline point, deg. F.	148	116	142	74
Liquid recovery, per cent by volume of charge to catalyst	97.7	96.3	96.3	100.2
32-deg.-A.P.I.-gravity furnace oil in catalytic gas oil, per cent	100	40.2	90	......

stock. Naphthas with a boiling range of 250° to 500° F. or gasolines with an end boiling point of 400° or 500° F. are used as the charging stocks and are pumped to a still where heating and vaporization take place at 850° F. The catalyst chambers receive the hot vapors, and after conversion has taken place the vapors are run through the heat exchangers to a fractionating tower where aviation gasoline, naphtha, gas oil, and gas are separated. The equipment for processing the reforming stock is the same as that used for cracking gas oils. Table 12 shows the yields of aviation gasoline from reforming operations, and Table 13 shows a gas analysis for the still gas from the process. The octane rating of the aviation gasoline produced is about 78 before the addition of tetraethyl lead; [10] when 6 cc. of tetraethyl lead are added, the rating is increased to 95 or 96 depending upon the stock to which it is added.

TABLE 12—AVIATION-GASOLINE YIELDS

Charge to Plant—Per Cent of Crude	*Straight-run Naphtha—Grade "B" Coastal Crude (Gravity, 29.7 Deg. A.P.I.) 30.9 (Initial)*	*Heavy Naphtha—East Texas Crude 19 to 39*
Aviation gasoline, per cent by volume	58.8	32.5
Motor naphtha, per cent by volume	18.8	53.0
Cracked gas oil, per cent by volume	9.1	
Dry gas, per cent by weight	13.1	13.7
Catalyst deposit, per cent by weight	2.3	2.4

TABLE 13—TYPICAL ANALYSIS OF DRY GAS

Gas	*Per Cent by Volume*
Hydrogen	5.4
Methane	9.9
Ethene-ane	6.1
Propene	6.1
Propane	20.8
*Iso*butane	5.0
*Iso*butene	0.5
*n*Butene	3.3
*n*Butane	42.9
Pentanes+	0.0
	100.0
Specific gravity (relative to air)	1.565

MOTOR FUEL FROM CRACKED GASES

Polymer Gasoline—In addition to the volume of cracked gasoline and other liquid products derived by the reforming and the cracking of oil, both by thermal and catalytic processes, approximately 350,000,000,000 cu. ft. of cracked gas are produced yearly. For a number of years the gas from the cracking reaction was utilized only as fuel under boilers and stills. The cracked gases contain olefinic hydrocarbons such as ethylene, propene, and butenes in addition to the

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[10] See Compound 103, Chapter 27.

saturated hydrocarbons such as methane, ethane, propane, and butanes. The commercial value of the hydrocarbon gases from the cracking process and natural gas has been greatly increased by the ever growing demand for high octane motor fuel.

When unsaturated hydrocarbons such as the olefines are subjected to high temperature and pressure with or without catalysts they can be made to polymerize to produce larger molecules. In some cases any of the saturated hydrocarbons which may be present will also enter into these polymerization reactions. In this way it is possible to take the small molecule hydrocarbons and produce liquid fuels. Moreover, the products which are so produced usually have very high octane numbers and, hence, are highly desirable for motor fuel. This fortunate circumstance makes it possible not only to conserve the petroleum supply by utilizing the still gases to produce more liquid fuel but also to produce a fuel of higher quality than has ever been possible before.

There are three polymerization processes in commercial use, two of which are thermal and use high pressure and the other is catalytic and operates at low temperature and pressure. In December 1940, there were 83 polymerization plants in the United States. The hydrocarbons present in the motor fuels produced by the thermal process are olefins, paraffins, cycloparaffins and aromatics.[11] The catalytic polymerization process produces a branched chain olefin gasoline.

The Unitary thermal process operates on cracked or paraffin hydrocarbon gases made up of propane-propene, butanes and butenes, operating under a temperature range of from 950 to 1100° F. and pressures of 1,000 to over 4,500 pounds per square inch. The liquid products are gasoline and gas oil.

Under these conditions of operation many complicated chemical reactions take place. There is undoubtedly a certain amount of cracking followed by the polymerization of the unsaturated compounds. The high pressures involved are conducive to the formation of polymers. This is in line with the Le Chatelier principle because the volume of polymerized products will be much less than that of the gases of small molecular weight which go to make up the heavier molecules. The conditions of temperature, pressure, and rate of flow which will give the optimum yield of the desired liquid products must be determined entirely by experiment because no adequate quantitative theory is available for predicting just what will happen in a set-up such as this.

The Multiple Coil thermal process operates on cracked and paraffinic gases at a temperature range of from 900 to 1300° F. under pressures varying from about 45 to 800 pounds per square inch. The olefinic hydrocarbons polymerized in the first reaction and the residue gas containing the paraffinic type are cracked in the second stage of operation. The olefinic hydrocarbons derived by the cracking of the paraffins are polymerized in the third stage of treatment. The three-stage process produces gasoline, fuel oil, and tar.

These two thermal processes for the production of polymerized gasoline were the ones that were first used. A number of rather large plants were installed and will probably be used for some time because of the investment involved. However, they may eventually be replaced by the more efficient catalytic polymerization processes.

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[11] For the chemical principles involved in these processes, see Chapter 3.

Catalytic Polymerization Process—The function of a catalyst is to promote a reaction at greater speed at a given temperature or to make a reaction go at a lower temperature than would otherwise be possible. Hence, the catalytic units can operate at lower temperatures and pressures than the thermal units, and additions can be adjusted to give much greater efficiency. It is also possible to get some molecular combinations which are not derived by the thermal processes. Another advantage is that such units can be made very small or very large and worked equally satisfactorily. This makes the catalytic units much more versatile and adaptable for all sizes of operating units. In December 1940 there were sixty-three U.O.P. (Universal Oil Products) catalytic polymerization units in commercial operation. The capacities of these units, processing cracked or olefin containing gases, range from 125,000 cu. ft. to 27,000,000 cu. ft.; or, on a gasoline (81 octane) production basis, from 18 bbl. to more than 2,500 bbl. daily. The polymerization plant shown in Figure 8 processes 2,500 bbls. of polymerized gasoline daily from 27,000,000 cu. ft. of cracked gas.

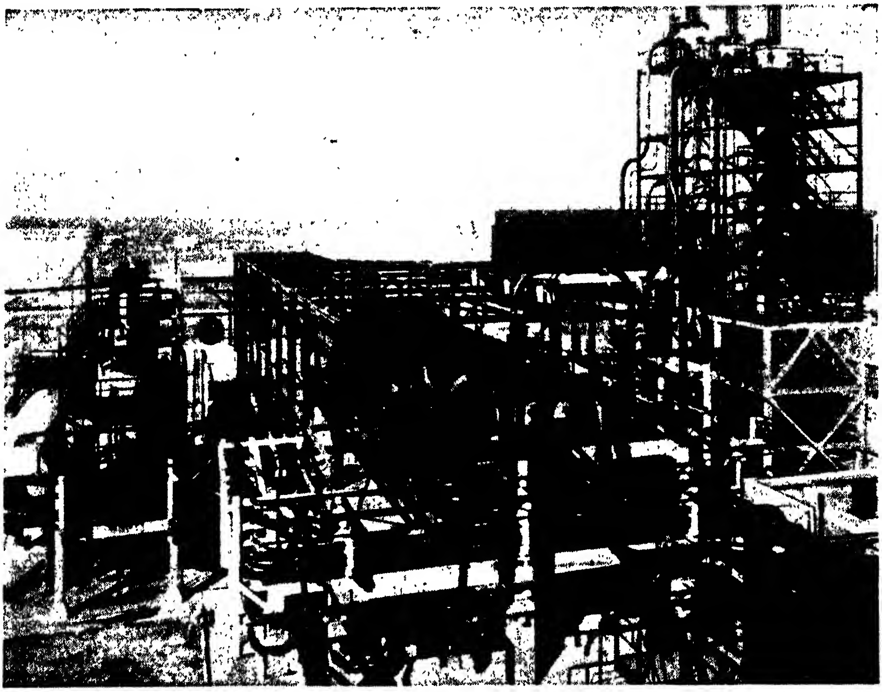

FIG. 8. Polymerization Plant Processing 27,000,000 Cu. Ft. Cracked Gas to Yield 2,500 Bbls. Poly Gasoline Per Day.

The combination of selective catalytic polymerization and hydrogenation units produces from 50 bbl. to 800 bbl. of isooctane fuel per day.[12] The increased yield of gasoline ranges from approximately 2 to 8 per cent, with an octane rise of 1 to 2 numbers on the refinery-gasoline output when processing naphtha, kerosene, gas oil, or topped crudes.

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[12] See p. 556.

Since these catalytic processes are the ones which will probably be the principal or sole producers in the future, the operation of one of these units will be described in considerable detail.

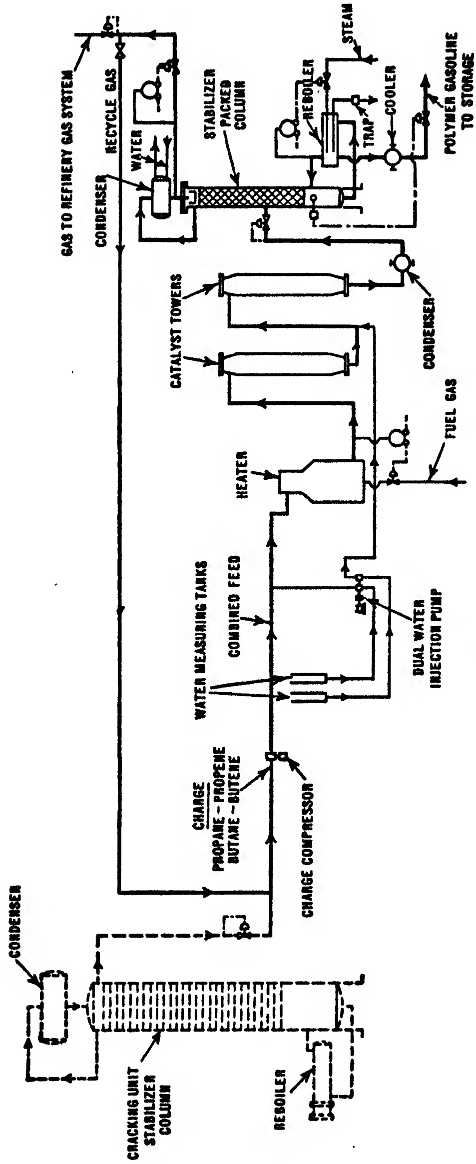

Fig. 9. Universal Oil Products Catalytic Polymerization Plant.

Polymerization Units—The midget catalytic polymerization units are particularly adapted to the small refinery due to the low cost of installation and the increased yield and quality of the gasoline produced. The cost of units processing cracked gas at the rate of 125,000 cu. ft. to 1,500,000 cu. ft. (arbitrarily called "midget units"; daily gasoline production, 18 bbl. to 215 bbl.) is approximately $15,000 to $35,000. Some of the midget poly units have paid installation costs in less than 40 days. The diagram of a large, selective catalytic polymerization unit is shown in Figure 9.

Catalytic poly units consist essentially of a heater, catalyst vessels, cooler, and a stabilizer. In order to minimize the size of the equipment required, and to obtain a long catalyst life, these units are operated at elevated pressures. As the charge to these small units is available either at separator pressure or stabilizer pressure, viz., at 50 lb. to 200 lb. per square inch, a compressor is also required.

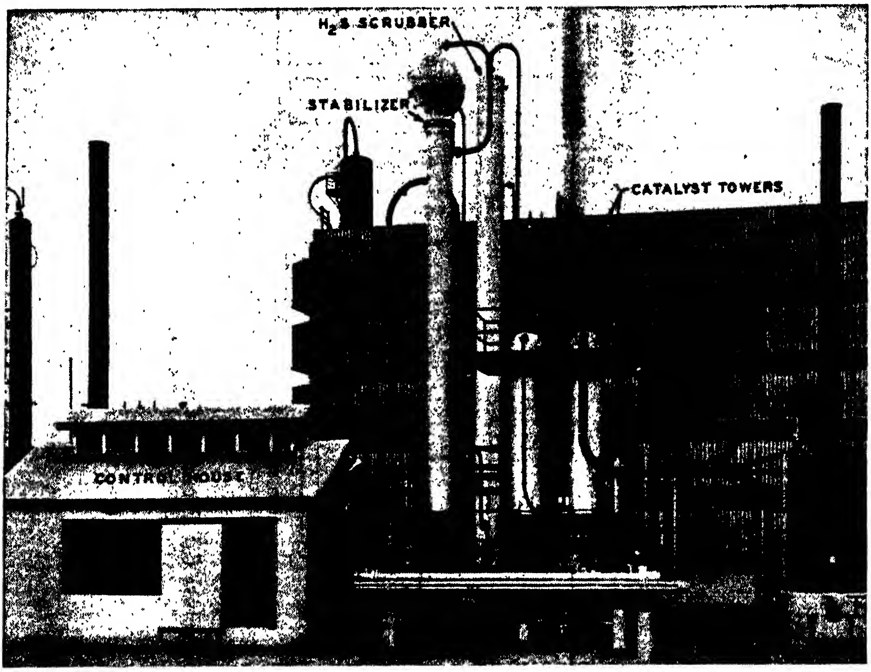

FIG. 10. Universal Oil Products Catalytic Polymerization Unit.

The material used in the construction of these units is standard in every respect, with no special alloys necessary. The stabilizers used are of a packed-column variety rather than the bubble-deck type.

In the operation of these units, the charge of the gases to the polymerizer is picked up by the compressor and discharged to a heater where the temperature of the gas is raised to 350 to 400° F. The heated gas then is passed in series through two tubes, usually made up of 24-in. pipe, filled with solid phosphoric-acid catalyst (a porous solid impregnated with phosphoric acid) upon whose surfaces the reaction takes place. The polymer product leaving the last catalyst vessel then is cooled to a temperature of 165° F. and discharged directly into the stabilizer, where the polymer, together with the amount of butanes required to give the desired vapor pressure, is separated from the balance of "spent gas." A schematic outline of poly units is shown in Figure 9 and an illustration is given in Figure 10.

The poly units are so constructed that operating conditions are maintained automatically, and the amount of control necessary is similar to that required by a stabilizer or an absorber. The compressor is hooked into the gas system, and the gas from the stabilizer discharged in such a manner that a constant gas flow is maintained throughout the system. The hook-up is arranged so the poly plant can be cut in or out at will without interrupting the cracking-plant stabilizing and gas-disposal system. Automatic controls are used to hold a constant inlet temperature to catalyst towers; a similar control is provided for the stabilizer reboiler. Pressures are regulated at the outlet of the catalyst towers and poly stabilizer. By proper manipulation of factors affecting catalyst-bed temperature, high olefin conversions and long catalyst life are obtained.

Composition of the Cracked Gases to be Polymerized—For the presentation of that composition of the feed, five catalytic poly units operating commercially were selected, having cracked gases containing from 19 to 41 per cent propene-butenes. These units are called: No. 1, 2, 3, 4, and 5 for the sake of identification.[18] The cracked-gas analyses for the five units are shown in Table 14.

TABLE 14—CRACKED-GAS ANALYSES

(Charging Stocks to Poly Units)

	1	*2*	*3*	*4*	*5*
Composition, mol per cent					
Hydrogen sulfide	0.15	1.8	0.33	1.0	0.35
Hydrogen	4.1	0.2	0.3	0.1	...
Methane	25.8	5.0	4.6	3.4	2.2
Ethylene	5.3	2.6	4.0	3.7	2.3
Ethane	16.9	18.9	20.3	16.4	10.7
Propene	15.0	17.1	17.9	23.4	17.8
Propane	23.3	44.1	29.5	27.8	25.1
n-Butenes	2.8	2.8	7.4	9.8	16.4
Isobutene	1.4	3.0	7.4	5.9	6.8
Butanes	4.6	5.9	11.9	10.0	17.9
Propene-butenes	19.2	22.9	29.4	38.2	41.0
Polymer gasoline (gallons per 1,000 cu. ft. of gas)	3.7	4.4	6.1	7.6	9.5

Effect of Hydrogen Sulfide—The charge to poly plant No. 1 is a mixture of the pressure-still receiver gas and stabilizer gas. The hydrogen sulfide content of these gases varies from 0.15 to 1.8 per cent. When hydrogen sulfide is present in cracked gases under catalytic polymerizing conditions, a reaction takes place with the olefins forming mercaptans such as ethyl, propyl, and butyl. When the sulfur content of the polymer gasoline is a factor to be considered, the gas should be freed of hydrogen sulfide before the polymerizing reaction.

Poly unit No. 2, processing gas high in hydrogen sulfide, produced a gasoline containing 1.5 per cent sulfur. In this case a means of treating was worked out which uses an absorber and the waste caustic from the refinery treating plant. When the sulfur content of the polymer gasoline is relatively high and waste caustic is not available, demercaptizing the polymer gasoline with strong caustic-soda solution may be cheaper than hydrogen-sulfide removal from the cracked

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[18] Shanley, W. B., and Egloff, G., American Petroleum Institute, New Orleans meeting, May, 1939.

gas. Polymer gasoline containing 0.3 or 0.4 per cent sulfur is used, as such, or blended with the gasoline produced in the refinery to bring the polymer product down to market specifications. In some parts of the country 0.4 per cent sulfur polymer gasoline is used and marketed with refinery gasoline containing a similar amount of sulfur.

Spent Gas—The cracked gases after the olefins have been polymerized into gasoline leave the stabilizer of the poly unit with a low olefin content. The cracked gas after being deolefinized is called "Spent Gas." Analyses of the spent gases leaving the stabilizers of the five poly units are shown in Table 15, the headings of which correspond to those of Table 14 of the initial cracked gas charging stocks.

TABLE 15—COMPOSITION OF SPENT GASES

	1	*2*	*3*	*4*	*5*
Composition, mol per cent					
Hydrogen	5.4	0.4	0.2	0.2	0.3
Methane	31.6	10.3	8.5	5.5	5.6
Ethylene	6.1	2.8	4.0	3.7	3.5
Ethane	24.6	34.1	30.2	29.8	25.1
Propene	2.2	3.4	2.1	4.6	0.8
Propane	22.9	46.0	41.9	49.8	50.7
n-Butenes	0.7	0.5	1.1	1.2	0.8
Isobutene	0.3	...	0.2	0.2	0.4
Butanes	6.2	2.5	10.2	5.0	11.6
Propene-butenes	3.2	3.9	3.4	6.0	2.0

The propene-butenes in the spent gases range from 2 to 6 per cent. The percentage of olefin conversion to polymer gasoline determined from the analyses in Table 15 and those given in Table 16 ranges between 85 and 95 per cent.

Olefin Conversion—In order that a clear picture may be presented of the olefin conversion effected by the five poly units, it is necessary to consider not only the olefins in the spent gas, but also the butenes dissolved in the polymer gasoline. In the case of the poly units under study, the average vapor pressure of the gasoline produced is 25 lb. per square inch. The butanes-butenes present in the gasoline average about 30 per cent of the high vapor pressure polymer. The olefin content of this C_4 fraction must be considered in determining the overall olefin conversion. Table 16 shows the olefin content of the C_4 fraction (normal and isobutane and normal and isobutenes) included in the polymer gasoline.

TABLE 16—COMPOSITION OF THE C_4 FRACTION IN POLY GASOLINE

	1	*3*	*4*	*5*
Composition, mol per cent				
Isobutene	1.7	1.5	2.5	1.4
n-Butenes	12.3	8.5	23.9	6.1
n- and Isobutane	86.0	90.0	73.6	92.5

Three butenes are usually present in cracked gases, butene-1, butene-2, and isobutene (2-methylpropene-1), in varying percentages; each has a different velocity of polymerization to gasoline under a given set of operating conditions. The isobutene polymerizes rapidly, butene-2 less so, and butene-1 with some difficulty. Poor conversion is evidenced by high normal butane in the butane-butene fraction. From the data in Table 16 it is apparent that the results obtained on poly unit No. 4 at the time the samples were taken and analyses made, were inferior to those of the other four commercial units. However, an olefin conversion to about 90 per cent polymer gasoline was possible by modifying the operating conditions.

Temperature Effects—Temperature affects the rate and degree of polymerization of olefin. The data are shown in Table 17.

TABLE 17—EFFECT OF CATALYST BED TEMPERATURE ON OLEFIN CONVERSION

° F.	*Olefin Conversion Per Cent*
406	76.5
415	82.0
421	80.5
423	84.4
428	88.3
429	90.0
445	92.8
452	95.0

Polymer Gasoline Yields—The percentage polymerization of the individual olefin hydrocarbons present in the cracked gases is shown in Table 18.

In poly units 4 and 5 the percentage of ethylene is 3.7 and 2.3; propene 23.4 and 17.8; n-butenes 9.8 and 16.4 and isobutene 5.0 and 6.8 are present respectively in the cracked gases. Under the conditions of commercial operation of the poly units, ethylene is relatively difficult to polymerize compared to propene and butenes. All of the olefins in the cracked gases could be polymerized but the product would boil largely outside the gasoline range. The data show that propene polymerizes readily, in both cases exceeding the average olefin conversion and exhibiting appreciably increased tendency towards polymerizing when compared with normal butene. In the case of unit four, the failure of normal butene to polymerize is chiefly responsible for the relatively low olefin conversion.

TABLE 18—PER CENT CONVERSION OF INDIVIDUAL OLEFIN HYDROCARBONS TO POLYMER GASOLINE

	4	*5*
Olefin, per cent		
Ethylene	44	35
Propene	89	98
Butene-1 and -2	71	92
Isobutene	97.3	94
Average per cent conversion (Propene-butenes)	85	94.9

It is evident that polymer gasoline yields based upon the cracked gas charging stock are dependent upon the percentage of propene and butenes present. The olefin content of the cracked charge to the five units under discussion range between 19 per cent and 41 per cent olefins. The yield of polymer gasoline based upon a 10 lb. Reid vapor pressure[14] ranges between 4.3 to 9.4 gallons per thousand cubic feet of gas charge to the units. These volumes of polymer gasoline show

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[14] The Reid vapor pressure is the vapor pressure of a liquid determined at 100° F. and given in lbs./sq. in., i.e. 4.3 Reid vapor pressure is 4.3 lbs./sq. in. pressure at 100° F.

an olefin conversion ranging between 85 per cent and 95 per cent. The higher yield is from cracked gas containing 41 per cent olefin. The gallonage of polymer gasoline represented by this period of operation is between 38 and 70 gallons per pound of catalyst.

Octane Numbers of Polymer Gasolines—The octane numbers of the gasolines produced in the five units under consideration are shown in Table 19.

TABLE 19—OCTANE NUMBERS OF POLYMER GASOLINES

	1	*2*	*3*	*4*	*5*
Octane number*	82	84.5	83.5	82.5	84
Blending octane number in 70-octane gasoline blends	90	...	94.5	88	97.5

* L-3 method.

The operation of these particular polymerization units has been described in considerable detail because it illustrates the principals involved in all polymer gasoline manufacture.

Although the character of the individual pieces of operating equipment may change in the years to come, the principles of catalytic polymerization of olefins to produce gasoline will undoubtedly be the same which are now being utilized in the five plants which have been discussed.

ISOOCTANE MOTOR FUEL

The polymer gasoline which has just been discussed has very good antiknock properties as is shown by the octane numbers running over 80 in Table 19. However, fuel of this quality is not sufficiently good for the very high compression-ratio motors which are used in modern aircraft. In order to supply the demand for very high quality fuel, the polymer gasoline processes have been refined and adjusted to produce a fuel which is practically pure isooctane, which by definition has an octane number of 100.

In principle, the octane plant runs upon a feed consisting of butane and butene, or sometimes on butene alone. Any butane which is present is cracked to butene during the first part of the operation. The butenes are polymerized to give isooctene. When hydrogen gas is introduced into the unit these octenes which are hydrogenated give isooctane which is the desired high quality fuel.[15]

Isooctane Units—The design of isooctane plants is such that it lends itself well to small units. Several midget isooctane units to produce 50 bbl. a day of isooctane have been designed. There are three selective polymerization units in commercial operation and one butane polymerization plant, the largest being about 800 bbls. per day.

Production of Crude Isooctene—The charge to the selective polymerization unit is a butane-butene fraction from the cracking still stabilizer. A typical analysis of the butane-butene fraction shows about 1 per cent propane and propene, 18 per cent isobutene, 33 per cent normal butene, and 48 per cent butanes.

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[15] See Chapter 3.

The butane-butene charge to the selective polymerization unit was analyzed as shown in Table 20.

TABLE 20—CHARGING STOCK TO SELECTIVE POLYMERIZATION UNIT

	Per Cent
Propane-propene	1.0
Isobutene	18.4
Normal butene	32.6
Butanes	48.0

Before passing to heat exchangers to remove the nitrogen and sulfur compounds present, this stock is water and caustic soda treated as shown in Figure 10.

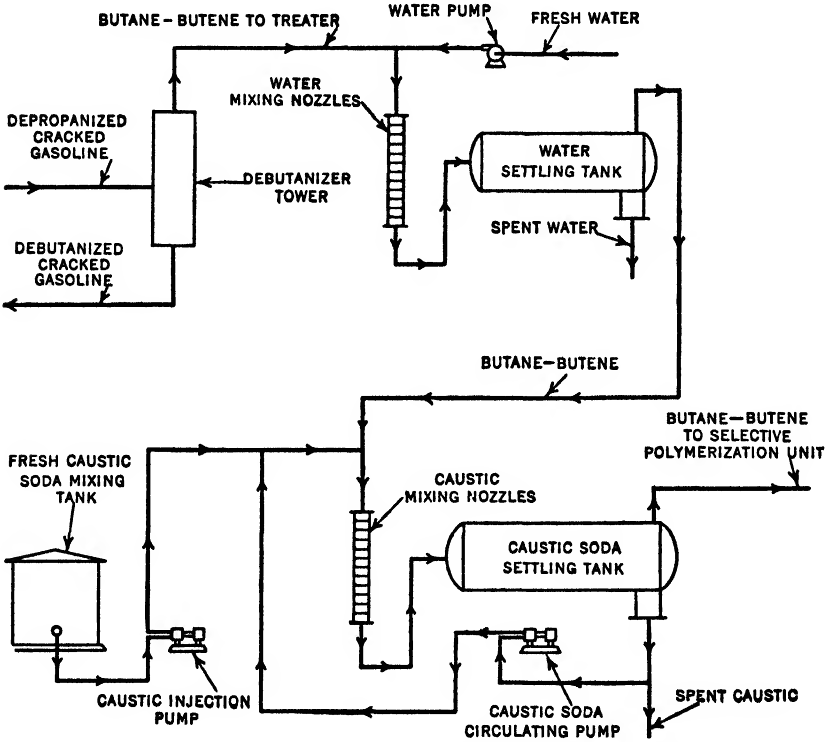

FIG. 11A. Butane-butene-water-caustic Soda Treater.

The temperature of selective polymerization ranges from 260° F. to 325° F. and the pressure is maintained at about 700 pounds per square inch. A flow chart of the butane-butene polymerization unit to produce isooctenes is shown in Figure 11. The temperature at which the selective polymerization takes place is an important factor which governs the octane rating and yield of the hydrogenated polymer gasoline. The crude polymer gasoline is made up of isooctenes, dodecenes and cetenes analyzed as shown in Table 21.

Treatment of Crudes—The crude polymer is distilled into an isooctane fraction and bottoms (heavy residue). The distillation and other properties of this fraction are shown in Table 22.

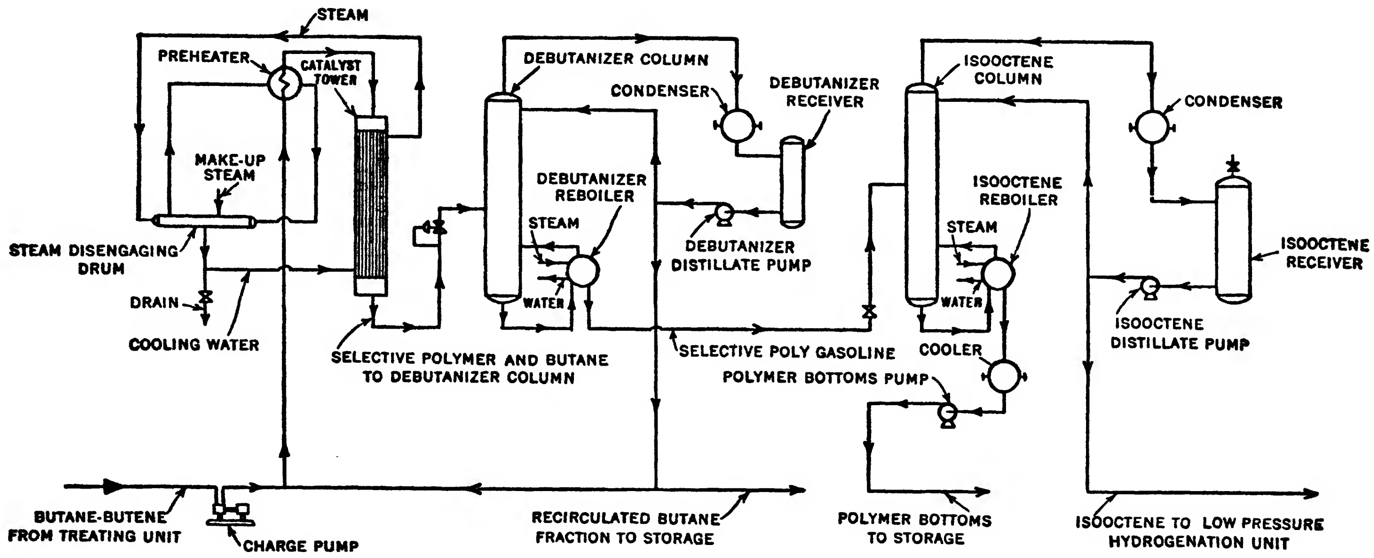

FIG. 11B. Catalytic Selective Polymerization Unit.

The polymer bottoms are made up largely of isododecenes fraction with a small proportion of isocetenes.

Yields—The conversion of isobutene is practically complete in the operating range of this process. The percentage conversion of normal butene increases; therefore the polymerization ratio of normal to isobutene will also increase. The yield of crude polymer increases under the same conditions, while its higher boiling components increase slightly. The finished hydrogenated isooctanes from the isooctenes produced at different temperatures (260° to 350° F.) may range in octane rating from 91 to 97. The olefin conversion to polymer based on the isobutene present in the gas will vary from 150 to 280 per cent on mole basis. The higher the octane rating of the hydrogenated polymer (isooctanes) the lower the yield based upon the butane-butene charge. The percentage conversion of the olefins in the butane-butene fraction to isooctenes is dependent upon the octane rating desired after their hydrogenation. The yield will vary between 24 and 31

TABLE 21—CRUDE SELECTIVE POLYMER

A.P.I. gravity	59.9
100 cc. distillation A.S.T.M.:	
I.B.P.	218
Per cent distilled over:	
10	225
20	226
30	228
40	229
50	231
60	233
70	236
80	242
90	261
End point	381
Octane number	84.0
Reid vapor pressure	1.3
Sulfur, per cent by weight (lamp)	0.005

TABLE 22—ISOOCTENES

A.P.I. gravity	61.5
100 cc. distillation A.S.T.M.:	
I.B.P.	200
Per cent distilled over:	
10	221
20	223
30	225
40	226
50	227
60	227
70	228
80	230
90	233
End point	267
Octane number (before hydrogenation)	85.5
Reid vapor pressure	2.0
Sulfur, per cent by weight (lamp)	0.002
Color	30+

per cent by volume of the charging stock given in Table 20. These polymer gasoline yields correspond to a 30-40 per cent yield by weight of the butane-butene fraction charged to the selective polymerization unit.

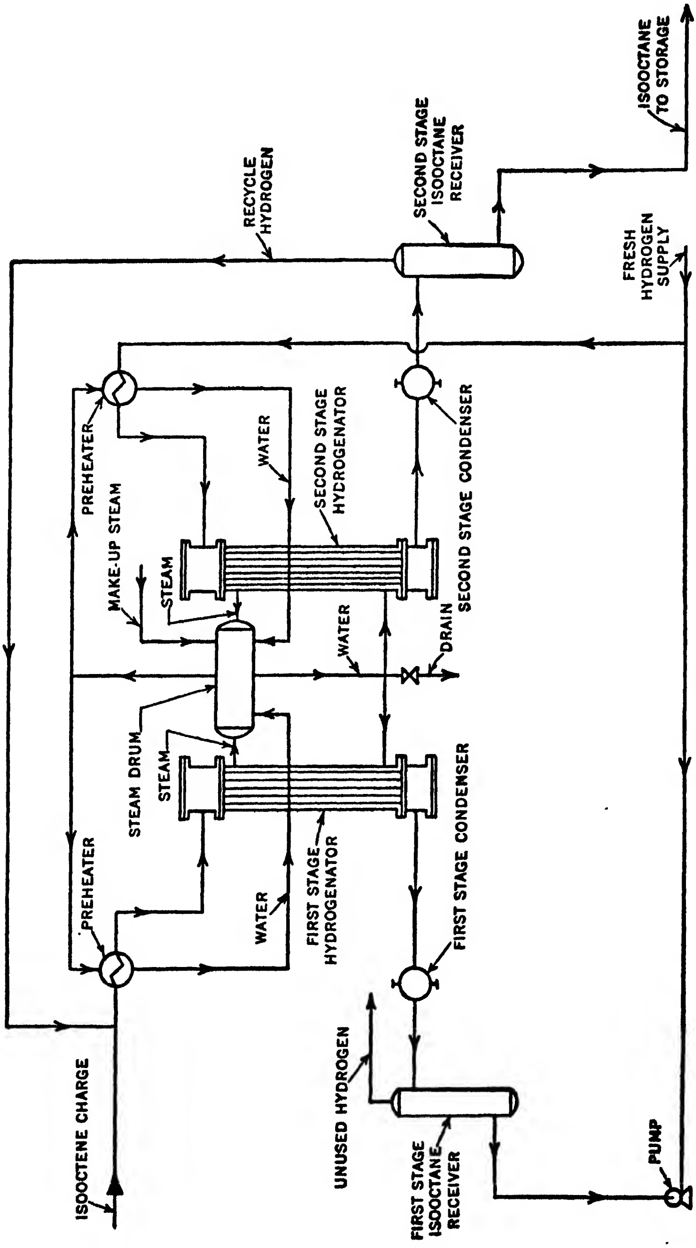

FIG. 12. Flow Sheet of Hydrogenation Unit.

Hydrogenation—The isooctenes produced may be converted into isooctanes by the U.O.P. low-pressure hydrogenation process at pressures of about 75 pounds and temperatures of 325° F. in the presence of a nickel catalyst. The hydrogenation reaction is exothermic; hence the unit is similar in design to the selective polymerization unit in the step of close temperature control by means of a water jacket around the reactor. A flow chart of the low pressure hydrogenation unit is shown in Figure 12. Figure 13 shows a polymerization installation.

FIG. 13. 500 Bbls. a Day Isooctane Unit.

The properties of the hydrogenated isooctanes are shown in Table 23.

TABLE 23—PROPERTIES OF ISOOCTANES

A.P.I. gravity	66.4
100 cc. distillation A.S.T.M.:	
I.B.P., ° F.	210
Per cent distilled over:	
10	222
50	227
90	232
End point	254
Octane number (A.S.T.M. motor method)	95.0
Reid vapor pressure (lbs.)	1.6
Sulfur, per cent	0.001
Olefins, per cent	0.5
Gum (copper dish)	0
Color	30

The isooctanes as produced are not aviation gasoline; they must be blended with aviation stock such as special straight-run or natural gasoline and isopentane to obtain proper volatility.

PRODUCTION OF MOTOR FUELS BY ALKYLATION, CYCLIZATION AND POLYMERIZATION METHODS

Alkylation—In the catalytic polymerization process normal butene combines with isobutene producing an olefinic polymer gasoline of lower octane rating than a branched chain paraffin. The olefinic polymer gasoline is hydrogenated into isooctanes of 95-100 octane. This is a two-stage process. A recently developed process, alkylation,[16] producing isooctanes in a one-step process is a catalytic one using sulfuric acid or aluminum chloride which combines isobutane with ethylene, propene, or butene forming isohexanes, isoheptanes, and isooctanes.

Sulfuric-Acid Alkylation—Alkylation is carried out by two methods in commercial practice, the thermal method at high pressure and the sulfuric acid method. The sulfuric acid process operates on isobutane and olefins.[17] Below 70° F. and under pressure, the olefins are absorbed on strong sulfuric acid; the reaction is rapid and cooling is necessary in order that it may be controlled. Normal paraffins are not absorbed on sulfuric acid, but isoparaffins are absorbed if the concentration of the acid is over 90 per cent. It is thought that the olefin forms an alkyl ester with the sulfuric acid and further reaction takes place forming the branched paraffin. The octane rating of the alkylated product ranges from 92 to 94. Figure 14 shows the flow diagram of the sulfuric acid alkylation process.

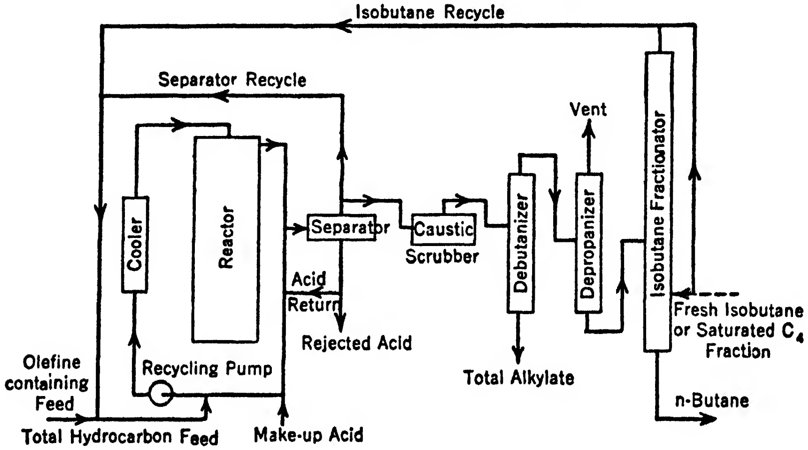

FIG. 14. Flow Diagram—Sulfuric Acid Alkylation Plant.

Manufacture of Neohexane—Isooctane may be considered a synthetic fuel with very desirable properties. However, as may be expected in such a complicated organic system as this, a great variety of other combinations are possible which might yield fuels just as satisfactory. One such new synthetic fuel is neohexane (2-2-dimethylbutane). Neohexane is particularly valuable because it has a higher vapor pressure than isooctane and hence is desirable for maintaining the desired fuel volatility.

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[16] For a discussion of the principles of alkylation, see Chapter 3.

[17] Anglo-Iranian, Humble Oil Refining, Shell Development and Texas Company, "Sulfuric Acid Alkylation," American Petroleum Institute, Chicago, Ill. (November, 1939).

Neohexane manufacture[18] from isobutane and ethylene takes place by means of thermal and pressure alkylation. Low olefin concentration and low conversion per pass is maintained in order to prevent polymerization from taking place. The operation occurs in two steps; the first is a cracking operation for the production of ethylene from an ethane-propane mixture while the second step

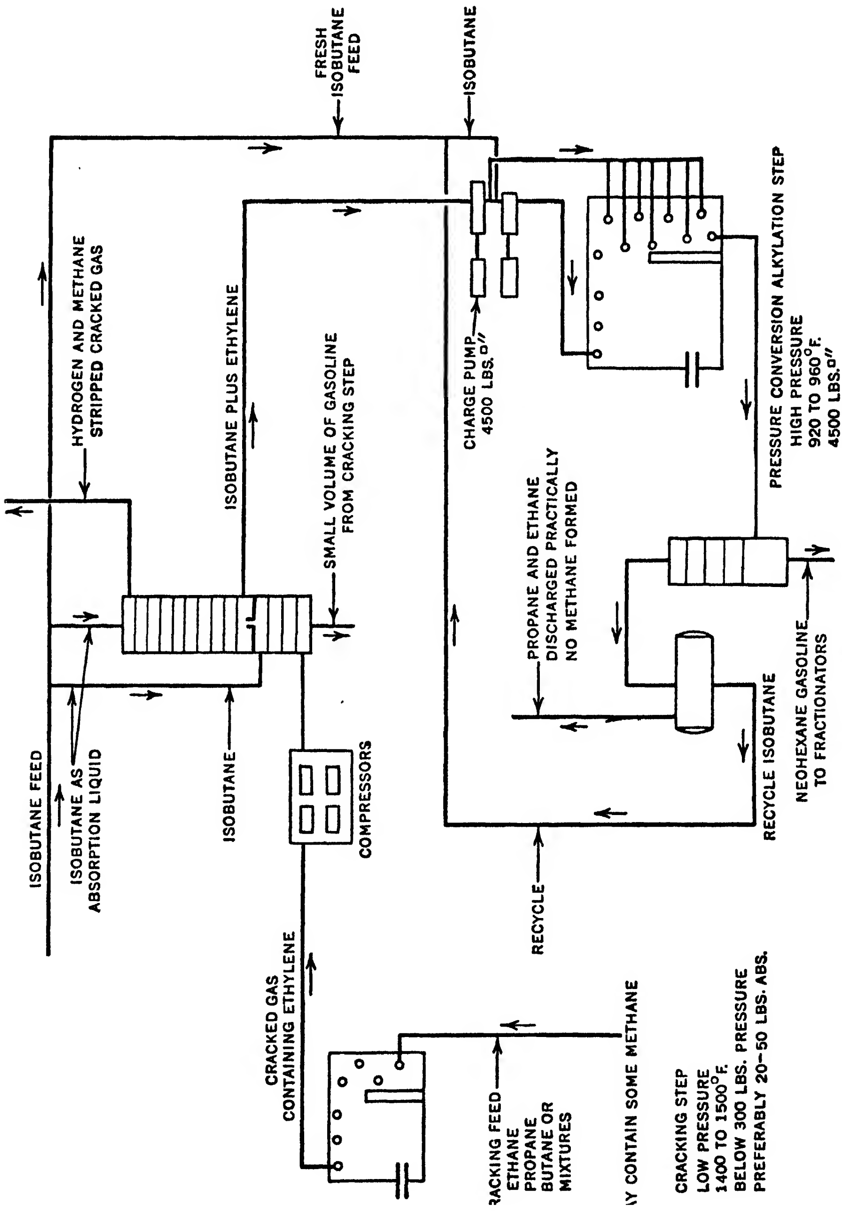

Fig. 15. Neohexane Pilot Plant.

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[18] Clarke, M. E., Chem. & Met. Eng., *47*, 225 (1940).

consists of alkylation of isobutane with ethylene at high pressure. Cracking is carried out at 1425° F. with pressure only a few pounds above atmospheric. During the alkylation step a 950° F. temperature is used with pressures ranging from 3,000 to 5,000 p.s.i. Some secondary reactions occur which yield hydrocarbons boiling above neohexane. The octane rating of neohexane is around 95, and because of the lower boiling point (121.5° F. for the pure material) in comparison to isooctane it is suitable for providing the proper aviation gasoline volatility. When the operation involves greater conversion per pass, the neohexane formed is not as pure a product as that from low conversion. The motor fuel from high conversion requires less fractionation and refining and is quite suitable for blending purposes. Figure 15 shows the flow diagram for the neohexane process.

Cyclization of Paraffins—Aromatic hydrocarbons are excellent blending hydrocarbons for increasing the octane rating of gasolines. The cyclization[19] of paraffin or olefin hydrocarbons to give aromatics may be effected by catalytically converting normal hexane, heptane, and octane (low octane rating) into benzol, toluol, and xylols (over 100 octane rating) respectively, with hydrogen as a byproduct, the yields being almost theoretical.

The lower-boiling hydrocarbons in petroleum, particularly those from Pennsylvania, the Mid-Continent, Michigan, and East Texas are predominantly straight-chain paraffins. By catalytic cyclization at 500° C. and atmospheric pressure these hydrocarbons may be converted into the corresponding aromatic hydrocarbons which have been obtained chiefly from coal tar heretofore.

The aromatic hydrocarbons are not so good for airplane use at present, although some tests indicate that they might become useful for that purpose. The cyclization of paraffins in petroleum to aromatics thus gives another enormous source of high antiknock motor fuels.

Isomerization[20] as a process has not been developed sufficiently to put into commercial use. However, when it is developed it will be a highly important process for converting low octane rating hydrocarbons to high octane fuels. This process would substitute in part, at least, for reforming gasolines into a high octane product. In the isomerization process there would be no loss of gasoline since the straight-chain paraffins would rearrange molecularly into branch-chain paraffins. A number of illustrations of this reaction follow:

Isomerization of Butane—The catalytic isomerization of normal butane to isobutane by the use of aluminum chloride takes place at 175° C. and 35 atmospheres pressure. Aluminum bromide at room temperature and 3 atmospheres pressure during a two months' period produced 78-82 per cent isobutane from n-butane at equilibrium conditions. Pentane of 64 octane number isomerized to 55.9 per cent 2-methylbutane of 91 octane rating at room temperature in the presence of aluminum bromide. Isohexanes were produced from n-hexane by the action of aluminum chloride. When normal heptane was studied, it was found that the temperatures of isomerization and polymerization were very close to each other. The amount of isomerization depends on the catalyst used; 85 per cent of normal heptane was converted into branched-chain heptanes at 420° C. during 3 hours.

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[19] For a discussion of the principles of aromatization, see Chapter 3.
[20] See Chapter 3.

Summary of High Octane Fuels—A number of methods for the production of high octane gasoline have been reviewed.[21] These methods consist of solvent extraction of straight-run and cracked gasolines, the edition of tetraethyl lead, and the blending of various hydrocarbons. The processes in use today for the manufacture of high octane fuels more nearly produce single hydrocarbons than any previously in use. The production of isooctane from both sulfuric acid alkylation and selective polymerization and the manufacture of neohexane by alkylation produce mainly the hydrocarbons designated.

The chemical structures of these hydrocarbons are responsible for their efficiencies as motor fuels. The 95 to 100 octane rating of these gasolines is responsible for about a 33 per cent power increase over older type fuels. Although only airplanes now use 95-100 octane gasoline, research programs in the oil industry aim eventually to enable all cars to use these fuels at a price level commensurate with ordinary gasolines of the present.

In the past twelve years, octane ratings of regular fuels have risen from 50 to 73. In terms of efficiency, this means about a 20 per cent increase. While the methods of manufacture have drastically changed, the price levels have been lowered about 7.5 cents per gallon, an annual saving to the motorist of about $1,500,000,000.

LUBRICATING OILS

Lubrication Theories and Definition—In any discussion of lubrication and lubricants a definition of terms is necessary. In any machine friction is encountered and, depending upon the type of work, may or may not be beneficial. There are three types of friction: starting, sliding, and rolling or, as sometimes classified, solid, rolling, and fluid. In a definition of lubrication a quotation from Chemical and Metallurgical Engineering[22] covers the subject.

"In a movement of any body, friction must be overcome by work . . . Lubrication is essentially the substitution of fluid friction for solid friction. The result is much like the discovery of early man that it was easier to float a log than to drag it."

The nature of surfaces is such that a cushion of oil is necessary to change the type of friction encountered between the two surfaces. An oiled surface gives a fluid type of friction which produces less heat than the solid friction between unoiled surfaces under load. The efficiency of the oiled surface depends upon the cohesive and adhesive properties of the oils used. Lubricants from various sources have been used, and these include animal, vegetable, and mineral oils. With the advent of heavier machines, operating at higher gear pressures, the older types of animal and vegetable oils were no longer suitable since they did not maintain their stability and cohesive and adhesive properties at high temperatures and pressures. Mineral oils, due to their abundance and stability under heavy service conditions are most widely used today. In order to meet the many and varying requirements of the motor car, lubricating oils must be processed and blended.

Solvent Extraction Methods of Refining Lubricating Oils—In the production of lubricating oils from petroleum, the first step is that of recovering

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[21] Egloff, Hubner, and Van Arsdell, Chem. Rev., *22*, 175 (1938).
[22] Chem. & Met. Eng., *47*, 172 (1940).

material in the correct boiling range for the particular lubricant. This is usually done as part of the regular refining operation as indicated by the various cuts from distillation tower shown in Figure 3.

Obviously, lubricants must be liquids of very low vapor pressure so the separation of one fraction of lubricating oil from another must usually be done under a vacuum, or by steam distillation.

Although no really accurate theories have been established as to the types of compounds which must be present in the lubricating oil to give the desired properties, a great deal of empirical information has been built up on this point. This field of information is much too complex to be gone into in the short space which can be allotted to petroleum in this volume but references may be found in the Reading List at the end of the chapter for those who wish to go into the details of the multitude of types and properties of different lubricating oils which are produced from petroleum.

In all cases before a lubricating oil can be considered satisfactory it is necessary to refine it by any one of various methods. The older methods consisted largely of treatments with H_2SO_4. Nearly all of the newer methods involve the operation of liquid-liquid extractions. The rest of this section on lubricating oils will be confined to a discussion of these methods of purification.

Processes for Refining Lubricating Oils—Modern processes for refining lubricating oils depend upon the selective solubilities of certain materials for the lubricating fraction of petroleum. The solvents used are liquid propane, furfural,[23] β,β'-dichloroethylether,[24] cresol base, nitrobenzene, phenol, and liquid sulfur dioxide. The processes are known as Furfural refining; chlorex, using β,β'-dichloroethylether; Duosol, using liquid propane and cresol base; nitrobenzene; phenol extraction; and the Edeleanu process using liquid sulfur dioxide. Flow charts for the furfural, chlorex, and Edeleanu extraction processes with their explanations are given in Figures 16, 17, and 18.

Furfural Refining Process[25]—"Furfural satisfactorily meets selective solvent requirements when employed in the lubricating oil refining process developed by the Texaco Development Corporation. The solvent selectivity ranks high among the commercially-available solvents; the cost of furfural is relatively low and, being manufactured from agricultural wastes, the supply is adequate. Furfural is relatively non-poisonous and no special precautions are taken in commercial handling of the solvent. The successful application of furfural to a wide range of lubricating oils has been demonstrated in several large commercial operating installations. The process is becoming widely adopted and a number of plants are operating and being installed at present.

"Furfural is employed normally in the extraction system at temperatures ranging from 150° F. to 250° F., at which temperatures practically any viscous or waxy oil can be readily handled. The oil viscosities at temperatures of application and a large difference in specific gravity between extract and raffinate[26]

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[23] See Compound 462, Chapter 27.

[24] See Compound 42, Chapter 27.

[25] Manley, R. E., and McCarty, B. Y., "Application of Furfural to the Refining of Lubricating Stocks," The Science of Petroleum, Vol. III, 192, Oxford University Press (1938).

[26] In liquid-liquid extraction parlance the "extract" is the liquid that dissolves impurities, the "raffinate" is the liquid that has been purified. For a discussion of the principles of liquid-liquid extraction, see Chapter 2.

solutions permit counterflow operation in a single packed tower, as well as counterflow operation in multi-stage at high charge and settling rates.

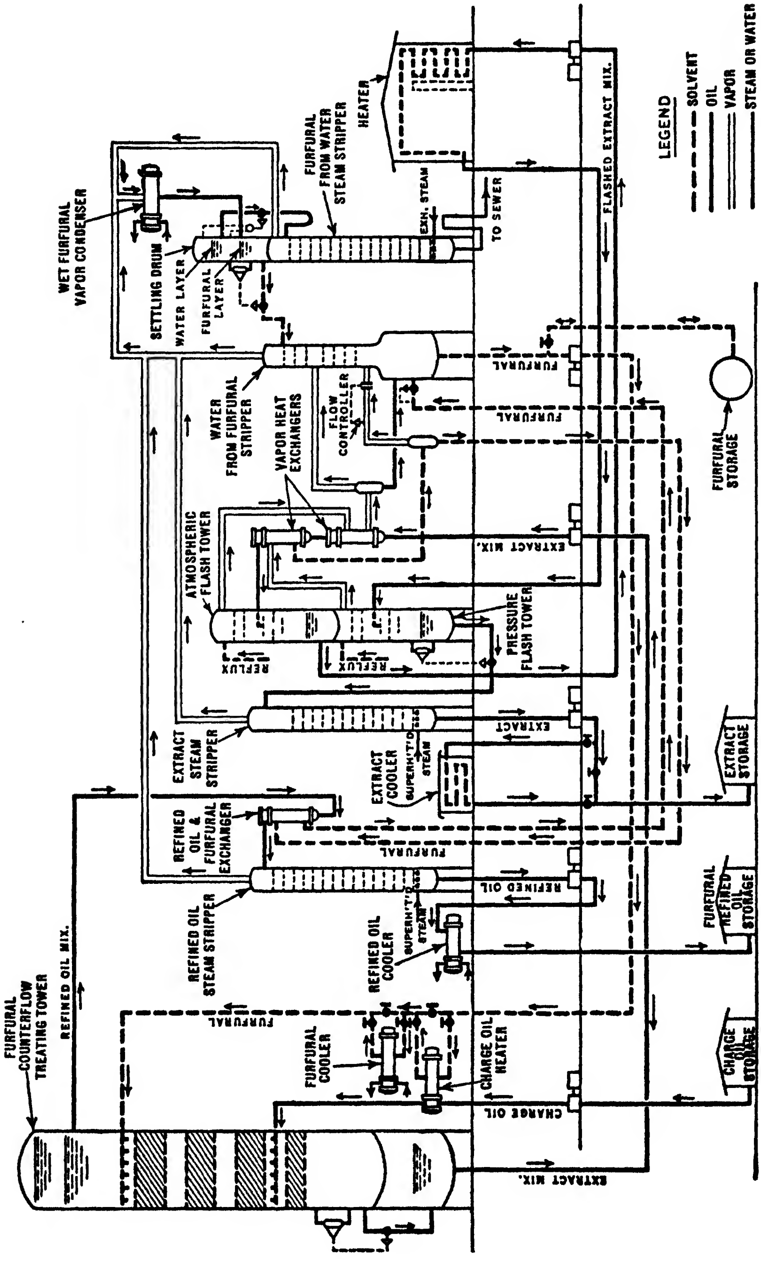

FIG. 16. Flow Sheet of Furfural Refining Process.

"The advantages of packed counterflow tower over a series of mixing and settling vessels are: Lower solvent and oil quantities in the system; lower initial investment; and lower operating and maintenance costs. A single counterflow tower with fifteen feet of packing is equivalent to more than ten stages of multistage counterflow, when furfural is used.

"Figure 16 reflects a typical layout of equipment employed in the process. Furfural, however, because of its stability over a wide range of operating conditions, lends itself to a variety of methods of recovery from raffinate and extract solutions. Different types of the solvent recovery systems have been developed in order to provide for maximum operating economy of each particular installation.

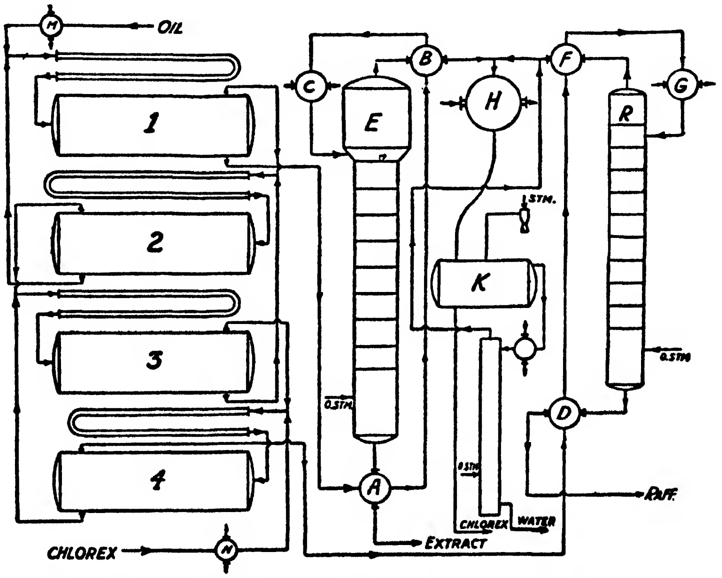

FIG. 17. Flow Sheet of Chlorex Process. (Courtesy Wurster & Sanger, Inc., Chicago, Ill.)

"The plant represented herewith comprises the following main operating units:

"1. Vertical counterflow extraction tower with suitable exchange and cooling equipment to provide means for charging solvent and oil at controlled, predetermined charge rates and temperatures.

"2. Surge capacity in the treating tower itself for storage of raffinate and extract solutions, prior to charging these solutions to respective solvent recovery equipment.

"3. Solvent-from-Extract recovery unit, including open steam stripper for removal of final traces of furfural from extract.

"4. Solvent-from-Raffinate recovery unit, including steam stripper.

"5. Solvent-from-Water recovery system, including settler and two fractionating columns. The settler is required to permit the mixture of water and furfural to separate into two layers; the lower layer being rich in furfural and the upper layer rich in water. One of the fractionating columns is employed in stripping water from the furfural layer, using furfural vapors as a stripping medium, and the second column is employed in stripping furfural from the water layer, using exhaust steam in the base of the column as heating medium.

"Untreated oil is charged to the bottom of the extraction tower at a predetermined temperature of from 150° F. to 200° F., while furfural at 200° F. to 260° F. is charged to the top of the tower, just below the surge space provided for accumulation of raffinate mix. Normal operation calls for a temperature gradient of from 20° F. to 50° F. between the top and bottom of the tower. The tower is maintained full of oil with the furfural flowing downward through the oil. Refined oil solution, containing only a small percentage of the furfural, flows from treating tower by gravity at a controlled rate to the steam stripper, where all furfural is removed from the oil.

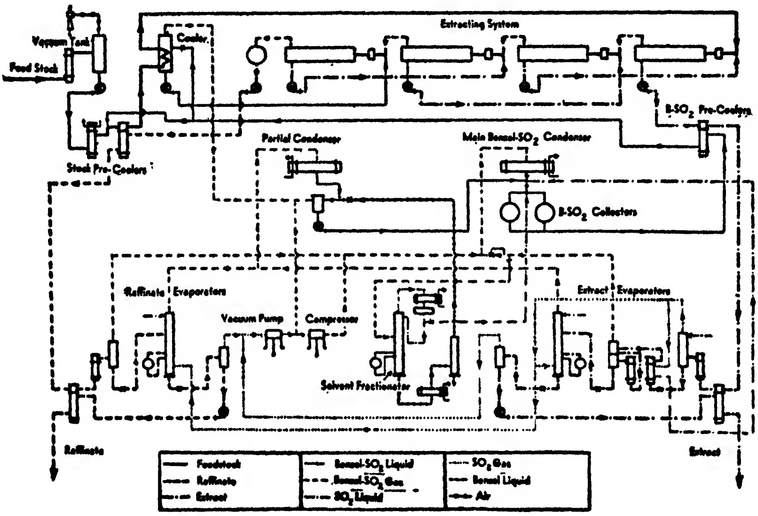

FIG. 18. Flow Sheet of Edeleanu Plant for Refining Heavy Lubricating Oils.

"The extract solution, containing the major portion of furfural, is pumped through heat exchangers to an atmospheric flash tower, where approximately 30 per cent of the furfural contained in the extract mix is vaporized. The flashed solution is then pumped through a fired heater to a pressure flash tower, where practically all of the remaining furfural is vaporized. The extract, and small percentage of furfural remaining in equilibrium, flows from the pressure flash tower to an atmospheric steam stripper, where all furfural is removed from the oil.

"Heat is recovered from the furfural vapors from both atmospheric and pressure flash towers by exchange with extract solution. Additional heat is recovered from the pressure condensate by exchange with the raffinate mix, after which pressure is released, and the furfural admitted to the main furfural charge accumulator, whence it is charged to treating tower.

"Vapor from the two steam strippers, together with vapors from the two fractionating columns, are condensed in a common condenser, and the condensate allowed to separate into two layers in the separating drum.

"The recovery of furfural from water is a very simple process, due to the fact that a constant boiling mixture of furfural and water has a lower boiling point than either pure water or furfural. For this reason a mixture of water and

TABLE 24—FURFURAL REFINING MID-CONTINENT DISTILLATES

	Light Mid-Continent Distillate				*Heavy Mid-Continent Distillate*				*Extra Heavy Mid-Continent Distillate*			
Ratio furfural to oil charged by volume	1.91				1.90				1.91			
Temperature tower top, ° F	200				235				240			
Temperature tower bottom, ° F	170				212				220			
Yield raffinate, % by volume	77.0				72.5				66.5			
Yield extract, % by vol.	23.0				27.5				33.5			
Inspection	*Raw Charge*	*Raffinate*	*Extract*	*Wax-free* Product*	*Raw Charge*	*Raffinate*	*Extract*	*Wax-free* Product*	*Raw Charge*	*Raffinate*	*Extract*	*Wax-free* Product*
Gravity, ° A.P.I.	25.6	30.8	11.2	28.6	23.1	28.6	10.7	26.5	20.8	27.1	10.3	26.2
Flash-point, C.O.C., ° F.	440	450	.....	450	500	510	.....	505	550	550	.....	555
Fire-point, C.O.C., ° F.	510	510	.....	510	80	575	.....	580	625	625	.....	630
Viscosity at 100° F. S.U.	.....	.....	.....	298	1,300	650	.....	932	5,000	1,220	.....	1,697
" " 130° F.	141	110	.....	....	......	281	.....	....	......	.....	.....	635
" " 210° F.	50	48	81	52	87	72	247	82	176	102	70 Furol	112
Carbon residue, %	0.27	0.03	.....	0.04	1.40	0.14	.....	0.25	3.70	0.40	.....	0.35
Colour	.....	.....	Black	100 (6-in. cell) Lovi.	......	.....	.....	40 (½-in. cell) Lovi.	Black	.....	.....	3 Tag.
Pour-point (A.S.T.M.), ° F.	90	100	.....	−5	110	115	.....	−5	+80	120	.....	−5
Viscosity index	72.5	105	.....	95	64	97	.....	87	54	97	.....	85

* Oils are finished with 3–7 lb. of acid per bbl., contact filtered and dewaxed by acetone-benzol process.

furfural is more volatile than either of the two substances in a pure state, and can, accordingly, be easily stripped from either."

Chlorex Solvent Refining Process[27]—"Chlorex (β,β'-Dichloroethylether) is a colorless liquid of ethereal and not unpleasant odor. Aside from the desirable property of high selectivity, this solvent is particularly well adapted to plant-scale usage. High specific gravity permits rapid separation of the two phases formed with oils. Its boiling point is well below the vaporization temperature of motor oils, and its low vapor pressure precludes the possibility of significant losses in storage. The freezing point of the material is so low that precautions are unnecessary. Since extraction with Chlorex is ordinarily carried out within the temperature range of 50° to 125° F. its low viscosity at these temperatures is a factor of importance. The flash point of the solvent is well above that considered hazardous. It is noninflammable at ordinary temperatures. It has been employed for nearly four years on plant-scale.

TABLE 25—PROPERTIES OF DICHLOROETHYLETHER

Structural formula, $Cl—CH_2CH_2—O—CH_2—CH_2—Cl$		
Boiling point (sea level), ° F. (° C.)	352.4	(178)
Freezing point, ° F. (° C.)	−60	(−51.7)
Specific gravity at 20°/20° C.	1.222	
Viscosity, centipoises at 25.5° C.	2.0653	
Viscosity, S.U. at 77° F. (25° C.) sec.	32	
Viscosity, S.U. at 32° F. (0° C.) sec.	39	
Vapor pressure at 100° F. (37.8° C.) mm.	2	
Latent heat of vaporization, B.t.u./lb. (cal./gram)	115.4	(64.1)
Specific heat at 85° F. (29.4° C.)	0.369	
Flash (closed cup), ° F. (° C.)	168	(75.6)
Solubility in water at 20° C., per cent	1.01	
Solubility in water at 90° C., per cent	1.71	

"Figure 17 shows a flow diagram of a Chlorex plant using the latest design of extraction equipment and vacuum distillation for continuous recovery of the solvent from the raffinate and extract solutions. Operation is as follows:

"The charge oil is pumped through a heat exchanger M, operated either as a cooler or heater, depending on whether water or steam is circulated through the unit. Chlorex-extraction temperatures range from 60 to 125° F., depending on the stock and the results desired. The rate of pumping the charge oil is under automatic flow control. The preheated or pre-cooled oil is mixed in the first-stage pipe mixer, with the extract solution (thrice-used Chlorex) from the second stage. This mixture settles in the first-stage settler is pumped, under automatic float control, to the extract-solution distillation unit for continuous recovery of the solvent. The raffinate solution from the first stage flows under first-stage pressure, and is mixed in the second-stage pipe mixer with extract solution from the third stage. This mixture settles in the second-stage settling tank. Raffinate solution from the second-stage settler is mixed with extract solution from the fourth-stage (once-used Chlorex) in the fourth-stage pipe mixer. This mixture settles in the third-stage settling tank. The raffinate solution from the third-stage settling tank is mixed with fresh Chlorex in the fourth-stage pipe mixer,

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[27] The Refinery Catalog, A Composite Catalog of Oil Refinery Equipment, No. 8, 410 (1939).

This mixture settles in the fourth-stage settling tank. The final raffinate solution from the fourth-stage is pumped under automatic control to the raffinate-solution distillation unit for continuous recovery of the solvent. When using more stages, the operation of the extraction equipment is the same as described above. A commercial countercurrent Chlorex extraction tower will shortly be installed in one of the Chlorex plants. This tower, which will be substituted for the countercurrent system of settlers and mixers, will have a treating capacity of over 1000 barrels of oil per day.

"A compact extraction unit is made by installing the horizontal settling tanks one above the other in structural-steel framework. The first (top) stage is maintained under the highest pressure, varying from 75 to 100 pounds per square inch. The pressure drops in increments of 10 pounds to 15 pounds per stage as the raffinate solution flows downward, while the extract solutions are pumped with float-controlled pumps in the opposite direction. Chlorex is charged to the system with an automatically-controlled pump through a heat exchanger, N, through which either water or steam may be circulated for heating or cooling the solvent.

"The solvent-recovery system is maintained under a vacuum of 26 inches to 28 inches mercury, and the solvent is completely recovered from the oil at a maximum stripping temperature of 300 to 325° F. The distillation equipment shown is steam-heated. Direct-fired vacuum-distillation units are also being used for recovering Chlorex, and the choice of equipment depends to a large degree on whether sufficient live steam is available to operate the unit.

"The final extract solution from the first-stage settling tank passes through a heat exchanger, A, utilizing the heat in the stripped bottoms from the extract-distillation unit, E. Further heat is supplied in a second heat exchanger, B, utilizing the heat in the hot Chlorex water vapors from the extract unit. Any additional heat required is supplied with a steam pre-heater, C. The extract solution enters the stripping column near the top. Open steam is applied at the bottom of the column. Re-boiler coils may be used to maintain the temperature throughout the column, which is a simple fractionating column with bubble trays.

"The final raffinate solution from the fourth stage is heated with bottoms and vapor heat exchangers, D and F, and a steam pre-heater, G. As the raffinate solution will contain only 15 to 25 per cent solvent, the raffinate-stripping unit, R, is smaller than the extract unit, E, where the bulk of the solvent is recovered. Hot Chlorex water vapors from the extract and raffinate-solution distillation units pass through a water-cooled condenser, H—the condensed Chlorex and water flowing to a settling tank, K, where the solvent is separated from the water by gravity and returned to storage. The water will be saturated with Chlorex with a solvent content of approximately 1 per cent. This water is fed through a preheater to a small, packed column, which may be readily constructed from a piece of casing. Open steam is added near the bottom. Water which is completely denuded of Chlorex flows to the sewer under automatic float control from the bottom of this tower, while the vapors which are rich in Chlorex pass to the raffinate-extract vapor condenser, H. A vacuum is maintained on the system by means of a steam-jet vacuum pump. It is not necessary to operate the water-stripping column under a vacuum. A Chlorex plant of this design, for treating 1000 barrels of oil per day, will require a total ground space not over 50 feet square. From 15,000 gallons to 20,000 gallons of solvent is adequate to place such a plant in operation."

Edeleanu Process[28]—"For refining lubricating oils of high viscosity the solvent power of the SO_2 is usually increased by adding benzol or another suitable aromatic solvent aid. The amount of benzol used in mixture with SO_2 depends upon the nature of the stock and the desired raffinate quality.

"The lube raffinates resulting from treatment with SO_2 or with a mixture of SO_2 and benzol are characterized by low carbon residue, excellent oxidation stability and high viscosity index. Edeleanu raffinates are finished by clay-contacting or re-running. Acid is very seldom required for finishing.

"SO_2 and benzol are easily recovered from the extract and raffinate at moderate temperature, and solvent losses are very low. Both solvents are, furthermore, exceedingly cheap.

"The flow diagram of a benzol-SO_2 plant for treatment of heavy lubricating oil is shown in Figure 18. The feed stock entering the plant flows through a steam heater into a tank held under vacuum, in which water and fixed gases are removed from the oil. From the vacuum tank the oil is pumped through a heat exchanger in which it is cooled by heat interchange with the cold raffinate solution coming from the extracting system. Before entering this exchanger the stock is diluted with mixed solvent. Final cooling of the stock is done by refrigeration in the combined stock and solvent cooling tank in which the stock passes through coils immersed in the solvent. The refrigerating effect is obtained through evaporating part of the solvent at atmospheric pressure. From this cooler the feed stock is pumped into the extracting system which consists of four mixers with settlers.

"The solvent recovered from extract and raffinate in the two evaporating systems is collected in the benzol-SO_2 collectors and flows from there through a heat exchanger in which it is pre-cooled by heat interchange with the cold extract solution coming from the extracting system. From said heat exchanger it flows into the above mentioned combined stock and solvent cooler where it is cooled down to the desired extraction temperature by direct evaporation. This tank cooler is held at about atmospheric pressure by means of compressors. From the solvent cooler the cold mixture of liquid benzol and SO_2 is continuously withdrawn by a pump which forces it into the last unit of the extracting system.

"The technical features of the multistage mixing-settling equipment are well known and need no description. The refined oil containing a certain amount of solvent flows from the last settler into a surge tank and from there it is passed into the raffinate recovery system. The extract solution is continuously withdrawn from the first settler and pumped into the extract evaporation system.

"The two solvent recovery systems have three stages in common, a flash stage operated at the pressure of the water-cooled solvent condenser, a stripper stage operated at about atmospheric pressure, in which the oil is stripped by means of SO_2 gas for the removal of the benzol, and a vacuum stage for the removal of the traces of SO_2 remaining in the oil after stripping. The extract evaporation system has furthermore a high pressure stage in which the bulk

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[28] The Refinery Catalog, A Composite Catalog of Oil Refinery Equipment, No. 8, 414 (1939).

of the SO_2 is removed from the incoming extract solution. The SO_2 overhead from the high pressure stage is partly used as stripping agent and partly condensed in a heat exchanger placed in the condenser pressure stage, in which the latent heat of the SO_2 vapors is utilized for reheating the bottoms from the high pressure stage.

"The solvent free extract and raffinate are passed through respective heat exchangers in which their heat content is utilized for preheating the cold raffinate and extract solution entering the recovery system.

"The SO_2 vapors expelled in the vacuum evaporators are compressed to the suction pressure of the compressors by means of gas pumps. The overhead from the strippers passes a partial condenser where most of its benzol content is liquefied. The non-condensed mixed solvent vapors are combined with the SO_2 gas from the vacuum stages and compressed to the pressure of the water-cooled main condenser by means of gas compressors.

"The plant shown in the flow sheet is further equipped with a solvent fractionator serving the purpose of adjusting the solvent composition suitable for the various kinds of stocks treated in the plant. This fractionator allows removal of any excess water that entered the plant with the feed stock and accumulated in the solvent."

BY-PRODUCTS

Research and development in by-products derived from petroleum during the past ten years have given the nation better and cheaper chemicals for all purposes. The list of chemicals from petroleum is growing in length and importance. Table 26 shows by-products derived from petroleum gases and other fractions. The products underlined are of major importance today from the standpoint of national self-sufficiency. (Table 26 is in pocket in back of volume.)

Prices of the chemicals derived from petroleum have steadily dropped since commercial production started. For instance the following quotation from the paper on "Synthetic Chemicals from Petroleum"[29] states:

"The production of alcohols, ketones, etc., from cracked petroleum gases has grown steadily in the past two decades. Thus, according to Tariff Commission reports, 37,500 gal. of isopropyl alcohol were made via the sulfonation of propene in 1922, 1,500,000 gal. in 1931, and 27,500,000 gal. in 1939. During this period the price fell steadily from $2.00 per gallon to 31 cents per gallon."

Synthetic rubber from petroleum is actually in production in several plants, since butadiene by dehydrogenation is readily available. Quantity production of the rubber is merely a matter of large scale development when and if advisable. The potential amounts of the butadiene available in the United States are about 80,000,000 tons yearly.

Benzene, toluene,[30] and xylenes potentially available from petroleum could supply more than 42.5 million tons of high explosives if necessary. From the standpoint of strategic materials, these explosives and the synthetic rubber could make the United States almost entirely independent of any outside country in these two fields.

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[29] Rosenstein, L., "Synthetic Chemicals from Petroleum," Preprint American Petroleum Institute Meeting, Nov. 13, 1940, Chicago, Ill.

[30] Chem. & Met. Eng., *47*, 535 (1940).

Glycerine manufacture[81] on a pilot plant scale from propene derived from petroleum is carried out by first chlorinating the propene at 500° C. to form chloride. After the formation of allyl chloride, hydrolysis to allyl alcohol followed by chlorohydrination and hydrolysis, or direct chlorohydrination of the allyl chloride with subsequent hydrolysis may be used in the pilot plant to produce glycerine. To produce glycerine from the allyl alcohol chlorine may be added directly yielding glycerine dichlorohydrin; however, this compound is not produced in sufficient quantity to give successful operation for the commercial manufacture of glycerine. Chlorohydrination in aqueous solutions yields glycerine but the process is not continuous. The amount of glycerine produced is about 93.5 per cent when the charge was maintained at 15° C. In order to get continuous operation the yield was maintained at 89.5 per cent of glycerine.

The glycerine produced in pilot plant operations meets commercial specifications. When pilot plant operation has sufficiently worked out the details of this process, commercial operation will doubtless follow since in this way sudden fluctuations in demand may be met without putting undue strain on the soap manufacturers who have heretofore furnished the greater amounts of glycerine required. In this process, also, both allyl chloride and allyl alcohol are of commercial importance so that glycerine manufacture could well be the source of these chemicals.

By-product industries have given the motor fuels discussed previously under polymerization, alkylation, and isooctane manufacture and in addition, alcohols, medicinals, cosmetics, paving and insulation materials. National economy is dependent on the actual products derived from petroleum, and much of the machinery of government depends upon the taxes derived from the oil industry.

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[81] Williams, E. C., Chem. & Met. Eng., *47*, 834 (December, 1940).

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CHAPTER 15

MANUFACTURED CITY GAS

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RECENT DEVELOPMENTS

In the early days of the industry, gas was employed primarily as an illuminant. At the present time, however, it is used almost exclusively for heating and its calorific value is the generally recognized statutory standard of quality.

While the earlier standards of calorific value called for from 575 to 600 B.T.U. per cubic foot, at the present time the tendency is toward lower values; i.e., from 500 to 535 B.T.U., while in England gas with calorific value as low as 430 B.T.U. is in use.

In the United States, the industry has undergone a rather marked revolution in practice due to the very greatly increased competition from fuel oil and from electricity. The introduction of small, easily installed oil-burning equipment and the development of the electric range and water heater have seriously affected sales for household use, in certain sections of the country, while the increasing use of electric heating has, for certain operations, been a serious competitor in industrial heating.

In addition to this type of competition, the extraordinary development in the long distance transmission of natural gas has resulted in the substitution of natural gas, either alone or admixed with manufactured gas, in cities more than a thousand miles from the gas fields.

As a result of these competitions the industry has found it necessary to promote new developments in order to maintain the market for its products. However, the use of gas for house heating and domestic refrigeration and the perfection of many new industrial applications have offset these losses and the gas industry looks hopefully to the development of important applications in air conditioning.

Technical developments have also wrought changes in the supply of raw materials with which the manufactured gas industry has to work. The great extension in the use of the cracking process[1] has caused a decrease in the supply with a consequent increase in the cost of the standard gas oil formerly used in the enriching of carbureted water gas, with the result that the gas industry has been forced to find means of utilizing fuel oils and other residual products from the oil industry, and in some instances has purchased the by-product oil gas resulting from these same cracking processes.

The greatly increased installation of by-product coke ovens which were built

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[1] See Chapter 14.

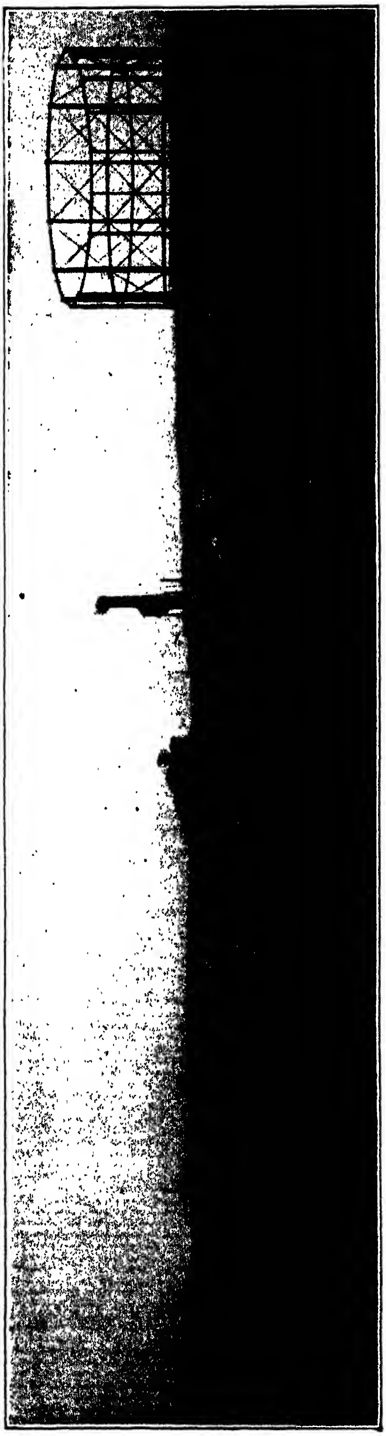

FIG. 1. General View of Coal Gas Plant from the Unloading of Coal to Gas Holders.

during or shortly after the first World War resulted in the availability of large supplies of coke oven gas, which was generally purchased as unpurified gas and was subsequently purified and distributed by the gas companies.

The net result of all of this has been that the gas industry has, to a considerable extent, changed its character from a strictly manufacturing industry to that of the distributor of a large proportion of gas as by-product from other industries. The extensive competition has driven the technologists to an intense search for every possible method of reducing their operating costs so that many new and efficient processes and developments are now in use, particularly in the manufacturing of carbureted water gas.

In Table 1 are given the comparative statistics of the gas industry for 1930 as compared with 1940. To some extent, these statistics are slightly misleading in that many cities which have changed over from the distribution of manufactured gas to the distribution of natural gas have been omitted as they are no longer manufacturers, and these statistics cover gas companies alone.

It will be noted how the proportion of gas purchased to the total gas sold has increased. The data also indicates the extensive use of natural gas in those districts where oil gas was formerly manufactured.

TABLE 1—STATISTICS OF GAS INDUSTRY

American Gas Association

	1930	*1940*
Population served (thousands)	45,665	48,376
Meters (thousands)	9,827	10,302
Customers (thousands)	9,666	10,167
Miles of main	78,800	92,000
Total sales (millions of cubic feet)	364,588	389,634
Revenue (thousands of dollars)	409,854	379,023
Gas Produced and Purchased		
Millions of Cubic Feet		
Carbureted water gas	193,806	173,427
Retort coal gas	37,458	15,645
Oil gas	4,711	6,065
Reformed natural and oil gas	2,205	9,942
Butane-air gas	1,529	84
Coke-oven gas produced	47,973	55,530
Coke-oven gas purchased	93,116	104,165
Oil gas purchased	1,976	4,846
Natural gas purchased	1,100	58,710
Percentage gas purchased	27.3	37.5
Raw Materials		
Thousands of Tons and Thousands of Gallons		
Anthracite coal	201	214
Bituminous coal	8,685	6,882
Coke and breeze	3,560	2,599
Petroleum oil	665,318	677,040

CONSTITUENTS OF MANUFACTURED GAS

In general, we may say that the commercial gases are mixtures of hydrocarbon vapors together with certain permanent gases produced by the pyrodecomposition and pyrosynthesis of the hydrocarbons comprising coal and oil, either alone or in the presence of air and steam. Commercial gases consist of mixtures, in varying proportions, of the gases or vapors whose characteristics are shown in Table 2.

TABLE 2—PROPERTIES OF THE IMPORTANT CONSTITUENTS OF COMMERCIAL GASES *
American Gas Association

Name	*Specific Gravity, Air = 1.0*	*Weight per Cubic Foot Pounds*	*Specific Heat*	*Heat of Formation B.T.U. per Pound*	*Heat of Combustion B.T.U. per Cubic Foot*		*Air Required for Combustion*	
					Gross	*Net*	*Cubic Feet per Cubic Foot*	*Pounds per Pound*
Illuminants								
Benzol	2.692	.2060	.375	− 229.3	3751	3601	35.732	13.297
Toluol	3.176	.2431	......	− 68.8	4484	4284	42.878	13.527
Xylene	3.662	.2803	......	+ 257.2	5230	4980	50.024	13.695
Ethylene	.974	.0746	.360	− 174.2	1613.8	1513.2	14.293	14.807
Propylene	1.450	.1110	.371	+ 138.0	2336	2186	21.439	14.807
Butylene	1.934	.1480	.362	+ 342.6	3084	2885	28.585	14.807
Hydrogen	.0696	.00533	3.409	....	325	275	2.382	34.344
Carbon Monoxide	.967	.0740	.245	+1869.2	321.8	321.8	2.382	2.471
Paraffin								
Methane	.554	.0424	.592	+2435.6	1013.2	913.1	9.528	17.265
Ethane	1.049	.0803	.413	+1713.6	1792	1641	16.675	16.119
Propane	1.562	.1196	.475	+1436.3	2590	2385	23.821	15.703
n-Butane	2.067	.1582	.459	+1317.3	3370	3113	30.967	15.487
Inerts								
Carbon Dioxide	1.528	.1170	.216	+3979.1	......	......	......	......
Oxygen	1.105	.0846	.217	....	......	......	......	......
Nitrogen	.972	.0744	.244	....	......	......	......	......
Air	1.000	.0766	.237	....	......	......	......	......
Steam	.622	.0476	.481	+6870.4	......	......	......	......
Impurities								
Hydrogen Sulfide	1.190	.0911	.242	+ 250.9	647	596	7.146	6.097
Ammonia	.596	.0456	.508	+1759.0	441	365	3.573	6.097
Cyanogen	1.800	.1378	.262	−2273.9	1238.2	1238.2	9.570	5.323
Carbon Disulfide	2.630	.2014	.159	−6160.0	1264.6	1264.6	14.355	5.466

* The data given are calculated to 60° F. and 30.0" mercury saturated. The English units, i.e., pounds, Fahrenheit degrees, and feet, since they are customary in the gas industry, are used in this chapter. In using tables giving the physical properties of gases care must be used to determine the conditions for which the table is calculated. Some tables are given with the gas reduced to the Continental Standards of 0° C. and 760 mm. pressure. Other tables are given at 62° F. and 30 in. The usual standards in the gas industry, however, are 60° F., 30 in. mercury, and saturated with water vapor. This results of course in a slight decrease in the heating values but is the condition under which practically all gas is actually handled in the laboratory.

In addition to the constituents shown in this table, there always exist in the crude gases, traces of ammonia and additional organic compounds, but the above-mentioned constituents may be considered as those important to the industrial chemist.

The relative occurrence of the commoner constituents in some of the many varieties of commercial gases is given in Table 3. These typical analyses must not be considered as standards, but as rather expressing the composition of commercial samples obtained under certain conditions with the process mentioned.

TABLE 3—COMPOSITION OF TYPICAL COMMERCIAL GASES

	Ills.	*CO*	H_2	CH_4	C_2H_6	CO_2	O_2	N_2	*B.T.U.*	*Sp. Gr.*
Coal Gas	4.0	8.5	49.8	29.5	3.2	1.6	0.4	3.2	622	....
Coal Gas	3.1	7.4	48.0	27.2	....	2.4	0.8	11.1	542	....
Coke-Oven Gas	4.0	6.3	46.5	32.1	....	2.2	0.8	8.1	584	....
Coke-Oven Gas	3.3	8.4	47.3	25.2	1.0	2.8	0.6	11.4	512	.51
Blue Water-Gas Coke	0.0	40.9	50.8	0.2	0.0	3.4	0.5	3.9	300	....
Blue Water-Gas Bit. Coal	1.1	32.1	46.9	4.5	0.0	5.1	0.2	10.1	317	....
Blow-Run Gas Coke	0.0	16.9	5.0	0.3	0.0	10.6	0.2	67.0	74	....
Blow-Run Gas Bit. Coal	0.5	24.2	10.9	3.0	0.0	4.5	0.4	56.5	154	....
Producer-Gas Coke	0.0	25.3	13.2	0.4	0.0	5.4	0.6	55.2	137	....
Producer-Gas Bit. Coal	0.2	17.6	10.4	6.3	0.0	7.3	0.7	58.1	161	....
Carbureted Water-Gas Gas Oil	9.8	29.5	37.6	11.4	0.7	5.9	0.6	4.5	528	....
Carbureted Water-Gas Heavy Oil	8.2	26.8	32.2	13.5	....	6.0	0.9	12.4	530	.66
Carbureted Water-Gas High B.T.U.	27.1	7.3	25.0	31.8	3.8	3.0	0.2	1.8	1080	.73
Mixed Gas	7.7	21.4	40.5	16.9	0.5	4.9	0.8	7.3	535	....
Mixed Gas	6.8	18.5	41.5	10.1	4.3	4.6	0.9	13.5	531	.60
Oil Gas—Pacific Coast	3.2	9.3	52.8	27.3	....	3.2	0.3	3.8	541	.41
Oil Gas—Pacific Coast	3.9	7.7	54.2	30.1	....	1.2	0.5	2.4	570	.37
Refinery-Oil Gas	7.9	2.1	7.8	19.7	44.3*	1.3	1.8	0.0	1472	1.00
Refinery-Oil Gas	10.3	1.5	4.4	73.9	....	0.9	1.9	7.1	1325	.90
Reformed Natural Gas	2.4	10.8	34.2	36.7	....	2.6	0.3	13.0	556	.53
Reformed Refinery-Oil Gas	3.5	17.9	53.0	17.3	2.4	2.5	0.1	3.3	530	.46
Natural Gas	0.0	0.0	0.0	96.7	0.0	1.0	0.0	2.3	977	.57
Natural Gas	0.0	0.0	0.0	80.5	18.2	0.0	0.0	1.3	1150	.65

* 15.1 Higher Paraffins.

GENERAL METHODS OF MANUFACTURE OF COAL GAS

The raw material of manufactured gas may be coal, coke or certain petroleum fractions, or various combinations of these. Coal gas was the earliest manufactured gas to be used commercially and Murdock, who was probably the inventor, distilled coal in a simple iron pot over a fire, and this is still the basic principle of our present-day practice.

At the present time bituminous coal is distilled in highly heated vessels made of fire clay or silica. While there is probably a greater number of plants that use retorts, the extension in the use of coke ovens has been such that probably the largest volume of coal gas is produced in ovens that have many times the capacity of the earlier retorts. Where retorts are used, as in the smaller plants, they are usually of the "D" section, varying considerably in their dimensions, length, and method of heating. They are usually set in groups of from six to nine retorts in what is known as a "bench," and the group of "benches," varying with the capacity of the plant, is known as the "stack." In a few of the older and smaller plants the retorts are heated by a direct fire of coke or coal, but in the more modern and larger plants they are heated with producer gas. These retorts may be set either in a horizontal or inclined position. The object, however, in any case is to drive off the volatile matter which consists principally of gas. Other products are also eliminated and will be considered in due course.

Many other methods of carbonizing have been proposed and tried. These may be classed under three heads, viz.: (1) the use of internally heated vessels; (2) the use of a body of ignited coke; and (3) the use of hot gas as a heat carrier. Many patents have been taken out and a great deal of experimental work has been done in endeavoring to perfect processes that would utilize these principles, but in general they have failed to produce a gas that could compete commercially with that produced in the usual system of carbonizing the coal in an externally-heated retort or oven. The principal causes of their failure have been the time required for the complete distillation of the coal and the poor quality of gas produced, due generally to its decomposition by the high temperatures that were necessarily employed.

With the present general use of the heating value standard and with the tendency towards lower heating values, interest has again been directed to processes using some of these principles, with considerable promise of success. A great deal of work is being done on what is known as complete carbonization, that is, the transformation of solid fuel entirely into gas and clinker in a single process. In the past, the low heating value of the gas so produced prevented consideration of such a process and at the present time it is necessary to enrich the gas made by such processes.

Methods of Distillation—There are three general methods by which the distillation of coal in externally-heated closed vessels is carried on:

First, the use of relatively small charges of coal which do not completely fill the enclosing retort, leaving a variable free space at the top. This would represent the usual horizontal or inclined retorts.

Second, the use of relatively large thick charges of coal which do not completely fill the retort and leave a free space at the top, such as a chamber or coke oven.

Third, the use of vertical retorts filled with the charge, where the whole periphery is heated. There may or may not be a free space above the charge at the top of the retort. This type includes the various continuous or intermittently charged vertical retorts and some of the modifications of the vertical coke oven.

Whatever the type of apparatus used, the production of coal gas is merely the process of the pyrolysis[2] of coal and the general principles are the same, no matter what the method.

Gas Coal—In the manufacture of coal gas, coal with a high volatile content is generally preferred; that is, a coal belonging to the bituminous series according to the usual method of coal classification.

These methods of classification vary somewhat, but usually depend either on the ratio of volatile combustible to fixed carbon, or upon the ratio of hydrogen to carbon, as determined by ultimate analysis.

In general, gas coals will have a volatile content of from 32 to 39 per cent with less than 10 per cent of ash and not over 1.25 per cent of sulfur. An English criterion is that the volatile matter should have a heating value equal

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[2] See also Chapter 3.

TABLE 4—CLASSIFICATION OF COALS BY RANK*—A.S.T.M.

Class	Group	*Limits of Fixed Carbon or B.T.U. Mineral Matter Free Basis*			*Requisite Physical Properties*
		Dry Fixed Carbon	*Dry Volatile Matter*	*Moist B.T.U.*†	
I. Anthracitic	1. Meta-anthracite................	98% or more	2% or less	....	....
	2. Anthracite................	92 to 98%	2 to 8%	....	....
	3. Semi-anthracite................	86 to 92%	8 to 14%	....	Non-agglomerating ‡
II. Bituminous§...	1. Low volatile bituminous coal.....	78 to 86%	14 to 22%	....	....
	2. Medium volatile bituminous coal	69 to 78%	22 to 31%	Moist B.T.U.	....
	3. High volatile A bituminous coal	Less than 69%	More than 31%	14,000 or more ‖	....
	4. High volatile B bituminous coal	....	....	13,000 to 14,000 ‖	....
	5. High volatile C bituminous coal	....	....	11,000 to 13,000 ‖	Either agglomerating or non-weathering ¶
III. Sub-Bituminous	1. Sub-bituminous A coal..........	....	....	11,000 to 13,000 ‖	Both weathering and non-agglomerating
	2. Sub-bituminous B coal..........	....	....	9,600 to 11,000 ‖	....
	3. Sub-bituminous C coal..........	....	....	8,500 to 9,500 ‖	....
IV. Lignitic	1. Lignite................	....	....	Less than 8,300	Consolidated
	2. Brown coal................	....	....	Less than 8,300	Unconsolidated

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* This classification does not include a few coals that have unusual physical and chemical properties and that come within the limits of fixed carbon or B.T.U. of the high volatile bituminous and sub-bituminous rank. All of these coals either contain less than 48 per cent dry mineral matter free, fixed carbon or have more than 15,500 moisture, mineral-matter-free B.T.U.

† Moist B.T.U. refers to coal containing its natural bed moisture but not containing visible water on the surface of the coal.

‡ If agglomerating classify in low-volatile group of the bituminous class.

§ It is recognised that there may be non-caking varieties in each group of the bituminous class.

‖ Coals having 69 per cent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of B.T.U.

¶ There are three varieties of coal in the high-volatile C bituminous coal group, namely variety (1), agglomerating and non-weathering; variety (2), agglomerating and weathering; variety (3), non-agglomerating and non-weathering.

to 150 B.T.U. per per cent. In addition it should produce a satisfactory coke and the ash should not be too low in fusing temperature.

While from a gas-making standpoint a high percentage of volatile matter is desirable, the composition of the volatile matter is of great importance. Experience has indicated that, in general, the newer mid-continent coals will yield less gas and of poorer quality than the older eastern coals with the same percentage of volatile matter.

TABLE 5—PROXIMATE AND ULTIMATE ANALYSES OF GAS COALS

	Pennsylvania	*West Virginia*	*Virginia*	*Kentucky*	*Illinois*	*Oklahoma*
Moisture	.71	1.47	1.43	1.35	6.57	4.76
Volatile combustible	34.50	37.12	35.39	36.00	33.51	36.13
Fixed carbon	58.18	55.34	60.59	58.10	53.29	54.41
Carbon	78.08	78.69	83.19	80.00	75.40	77.32
Hydrogen	5.15	5.45	5.28	5.25	4.88	5.45
Oxygen	7.59	6.95	7.05	8.40	10.56	9.36
Nitrogen	1.63	1.69	1.49	1.30	1.55	1.65
Sulfur	.94	1.15	.40	.50	.48	1.32
Ash	6.61	6.07	2.59	4.55	6.63	4.90
Heating value, B.T.U.	14256	14250	14724	14200	12480	13157
Fusing point ash, ° F.	2580°	2280°	2450°	2340°	2175°	2250°

This is partially explained by the ultimate analysis where it will be noted that the eastern coals are lower in oxygen than the mid-continent coals and, therefore have a higher available hydrogen—i.e., $\left(H - \frac{O}{8}\right)$, and generally increasing percentages of hydrogen results in a greater yield of gaseous products.

On the other hand, increased percentages of oxygen lower the gas yield, give poorer tar, and gas of lower heating value.

The presence of sulfur in coal is generally to be avoided as far as possible, yet its manner of occurrence is important in determining whether it will be volatile and go off in the gas and have to be removed by purification or whether it will remain in the coke. The work of Parr and Powell in differentiating the forms of sulfur as it occurs in the coal, into organic, inorganic, and pyritic sulfur was of great value in this connection. Where the coke is to be used for the manufacture of water gas, the composition and fusing point of the ash is important, while in case it is to be used for foundry work, the absence of sulfur and phosphorus is essential.

An important quality of the coal, especially for use in coke ovens, is the question as to whether or not it swells during the carbonization. Some coals will swell and develop such pressure that the walls of the retort are actually sheared up and even slightly swelling coals may be almost impossible to remove from the oven due to the coke being forced into the interstices and joints in the oven wall.

Theory of Coal Carbonization—The carbonization of bituminous coal might be expected to be slightly endothermic. The earlier work done on the process indicated that it was slightly exothermic, but the more recent work shows that the net heat quantity involved, excluding sensible and latent heat, is so small as to be almost within the limitation of experimental error, so it is probably slightly endothermic, at least in coke oven practice. Apparently net reaction heat is influenced by the nature of the coal and the method of carbonization employed.

Apparently the primary reactions are endothermic up to 800° F. Then there is an exothermic period, possibly followed by an endothermic period, although English experimenters believe that above 1200° F. the reaction again becomes exothermic. The results of different experiments range from 350 B.T.U. per pound absorbed to the same amount given off.

The fuel used in carrying out the process serves to start the distillation and supply the sensible heat that is carried off by the evolved products. From the heat balance that is given in Table 6 it will be noted that the heat given off by the reaction is but a small fraction of the total heat involved and may be neglected.

TABLE 6—TYPICAL HEAT BALANCE WITH A REGENERATIVE BENCH

Basis: 100 lbs. of Coal Carbonized

HEAT PRODUCED	*B.T.U.*
By combustion of coke	180,553
By formation of volatile compounds	52,637
Total heat evolved	233,190

HEAT ABSORBED	*B.T.U.*
As sensible and latent heat of flue gases	58,734
As sensible heat of gaseous vapors	32,166
As sensible heat of coke	43,148
As sensible heat of clinker	1,863
By radiation	48,276
By formation of volatile compounds	3,517
By decomposition of coal	45,486
Total heat absorbed	233,190

PERCENTAGE DISTRIBUTION OF HEAT LOSSES	*Per Cent*
By flue gases	25.20
By volatile compounds	13.80
By coke	18.50
	57.50
By radiation	20.70
By formation of volatile compounds	1.50
By decomposition of coal	19.50
By clinker	.80
	42.50

The general course of the distillation of coal is influenced by a number of factors and these may be summarized into the general statement that under any given condition of temperature and pressure the rate at which the heat penetrates the coal particles and the length of time the vapors are exposed to elevated temperatures determine the course and results of the distillation.

Rate of Carbonization. The coal particles acquire the temperature of the retort by conduction, radiation, and from the passage of the heated vapors through the charge. The rate of carbonization toward the center of a charge has been estimated at from 1.0 to 1.5 inches per hour in horizontal retorts, 0.5 to 0.6 inches in vertical retorts, and from 0.3 to 0.5 inches in coke ovens. The factors that influence the rapidity of heating are the available heat, the size of the coal particles and the moisture content. In general, in order to secure the maximum increase in temperature, the coal particles should be brought into intimate contact with the walls of the retort. A certain percentage of voids for the circulation of the heated gases must be provided. An increase in the size of the coal particles up to a certain point generally yields improved results.

Chemical Aspects of Coal Carbonization—*First Stage.* There is a preliminary endothermic decomposition which begins as soon as the coal has reached a temperature of 650° to 750° F. At this stage the coal assumes a plastic state.

Second Stage. The products resulting from the fusion of the coal in the first stage, consisting largely of higher members of the aliphatic series, suffer molecular rearrangement with the formation of a very complex set of hydrocarbons as exemplified by low-temperature tar, while the gaseous products will be compounds containing probably not over three atoms of carbon.

Third Stage. The vapors resulting from the second stage, when removed from the protecting influence of the coal particles, are acted upon by the heat conducted and radiated from the more highly heated portions of the charge proper, the sides of the containing retort and the highly heated surfaces with which the vapors may come into contact.

The reactions that take place during the third stage are very complicated and depend upon the temperature, time of contact and pressure. These factors are so intermingled that it is difficult to give each its true value as effecting the whole.

The distillation of coal yields four classes of products: gases, condensed watery solutions, condensible hydrocarbons and a carbonaceous residue.

These products are known commercially as coal gas, ammoniacal liquor, coal tar and coke. The average distribution of the elements in the coal into these products with their ultimate analysis is given in Table 7.

If we should express the ultimate composition of these products as complex molecules the decomposition of the coal might be represented by the following equation:

$$\underset{\text{Coal}}{C_{357}H_{281}O_{39}} = \underset{\text{Coke}}{C_{280}H_{26}O_8} + \underset{\text{Tar}}{C_{27}H_{22}O_2} + \underset{\text{Gas}}{5C_{10}H_{41}O_3} + \underset{\text{Water}}{14H_2O}.$$

If the heats of combustion are calculated by the Dulong formula it will be found that the sum of the heats of combustion of the products is less by some 2.42 per cent than the heat of combustion of the coal, so that the reaction is exothermic by about 339 B.T.U. per pound of coal, which represents the heat liberated and thus lost during the distillation.

The relative occurrence of the constituents of these products is in general dependent upon the complex reactions that take place in the third stage of the carbonization. As these products are evolved as vapors, we may consider them together and discuss later the different products formed by condensation.

The study of the mechanism of the coal carbonization has been greatly aided by the experimental work on the composition of the coal substance and the effect of varying degrees of temperature on the coal itself and on the components which are separable by the use of organic solvents. In this manner two main fractions can be separated, the one probably related to the original cellulose and the other to the resinous constituents of the coal. These complex organic materials seem to correspond closely to the light tars or oils produced by the distillation of the coal at low temperatures in a vacuum. They usually show a very large percentage of phenolic bodies, together with a trace of aromatic hydrocarbons. When these oils are subjected to temperatures ranging from 550° to 800° C. there is a progressive decomposition of the olefines and higher paraffines and naphthenes and an increasing production of aromatic hydrocarbons.

TABLE 7—TYPICAL ULTIMATE ANALYSIS OF THE PRODUCTS OF COAL DISTILLATION

	Coal	*Coke*	*Tar*	*Gas*	*Liquor*
Ash	8.18	8.18	......	......	......
Moisture	4.34	......	......	......	4.340
Carbon	72.08	56.453	5.418	10.209	......
Hydrogen	4.78	.446	.378	3.481	.475
Oxygen	8.73	.909	.504	3.516	3.800
Nitrogen	.87	.271	.042	.374	.183
Sulfur	1.02	.712	......	.308	......
Totals	100.00	67.071	6.342	17.888	8.799

The Formation of Aromatics. At the present time there are three general viewpoints in connection with the formation of the aromatic hydrocarbons:

1. The formation of aromatic hydrocarbons proceeds through a preliminary decomposition of the large molecules and a subsequent building up. This point of view is held by Bone, Jones, and others.

2. The phenols are primary products and that these lose alkyl groups and are hydrogenated. This view was originally put forth by Schultz many years ago and is now supported by Fisher and Schrader, Morgan, Soule, and others.

3. That unsaturated naphthenes are primary products and that the aromatics are formed from these by the splitting off of hydrogen and alkyl groups.

There has been a tendency to ascribe to the naphthenes an important part as intermediate products in these secondary transformations, but in view of our present knowledge it appears more likely that the higher members of the olefine series are probably of great importance, because the naphthenes appear to break down at somewhat lower temperatures than those at which practice indicates the maximum formation of aromatic hydrocarbons takes place.

If we assume that the product of the first two stages in the carbonization may be typified by the tar produced by low temperature distillation, we would have paraffines, naphthenes, higher olefines and phenols as principal products. When these products are subjected to increasing temperatures we probably have reactions similar to all three of the previous theories taking place at the same time.

Effect of Temperature. At the lower temperatures, olefines, paraffines, and unsaturated hydrocarbons predominate. As the temperature is increased, paraffine hydrocarbons disappear and the unsaturated hydrocarbons diminish and the higher homologs of benzol appear. With increasing temperature, the lower homologs of benzol become more important. With further increasing temperature, benzol becomes the important homolog and the higher aromatic compounds, such as naphthalene and, later, anthracene, begin to increase. These complicated reactions are reflected in the gas by showing a decreasing percentage of illuminants (benzene homologs and olefines up to butylene), decreasing ethane, and increasing methane and hydrogen.

TABLE 8—EFFECT OF DIFFERENT CARBONIZING TEMPERATURES

Temperature	*800° F.*	*1000° F.*	*1200° F.*	*1400° F.*
Yield, cubic feet per pound	.409	1.233	2.319	3.601
B.T.U. per cubic foot	523	651	745	626
B.T.U. per pound	214	803	1728	2254
Tar, gallons per ton	12.6	23.8	22.4	28.6
Coke, per cent	78.8	69.5	67.8	66.95
Volatiles in coke	22.04	13.00	7.97	5.88
Ammonia, pounds per ton	.37	1.47	2.29	3.71
Oils	6.00	5.85	5.75	4.50
CO	4.00	4.90	4.70	7.30
H_2	19.66	22.03	32.13	39.70
CH_4	18.45	30.78	36.53	37.30
C_2H_6	8.02	7.84	8.27	1.60
CO_2	7.80	6.00	3.45	3.20
O_2	.60	.30	1.20	1.35
N_2	35.47	23.23	7.97	5.05

Table 8 gives the results of actual conditions in carbonizing as affecting the composition of the gas, tar and coke at different periods of the distillation and under different temperature conditions.

The effect of the proper and regulated amount of superheating is well shown by the superior results obtained with the American type of vertical retorts which are not completely filled, the upper 4 to 5 ft. of the retort acting as a fixing chamber as against the German type in which the retort is completely filled and no fixing surface exists.

It will be noted that as the temperature rises and the time of exposure increases (due to the small make of gas), the change and the character of the products closely follow the directions that the experimental investigations have predicted, i.e., the gradual decrease in the olefines and ethane and the increase in the methane and hydrogen.

Effect of Pressure. The pressure at which these reactions take place has a considerable influence on the products formed. Owing to the permeability of the retorts if too low a pressure is maintained, furnace gases will be drawn in, which would seriously lower the heating value, while on the other hand an excessive pressure, by retarding the evolution of the gas, tends to result in excessive decomposition and in the formation of graphitic carbon. Experience points generally to a balanced pressure just equal to that of the atmosphere, and it should be maintained as nearly constant as possible. This latter condition is probably best insured by the use of retort house governors.

Variations During Distillation Period. It will be noted from the foregoing that the gas obtained from a pound of coal and its heating value depend upon a number of factors, viz., the coal, the system of carbonization employed, the temperature in the retorts, and several other conditions.

TABLE 9—VARIATIONS DURING DISTILLATION

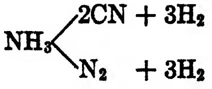
Vertical Retorts

Hours After Charging	*1st*	*2nd*	*3rd*	*4th*	*5th*	*6th*	*7th*	*8th*	*9th*
	%	%	%	%	%	%	%	%	%
Proportion of yield	16.8	14.1	13.0	11.9	11.7	11.2	9.6	6.5	5.2
Heating Value in B.T.U.	701	765	707	678	625	597	542	446	400
Ammonia, grains per 100 cu. ft.	540	440	380	250	250	250	130	70	40
H_2S, grains per 100 cu. ft.	510	470	430	295	285	260	180	100	50
Ills.	8.05	8.00	7.70	5.60	4.10	3.60	2.80	.80	.30
CO	8.90	7.20	8.40	8.60	7.05	8.60	7.70	7.60	6.30
H_2	38.25	37.80	36.80	39.00	44.15	45.80	57.40	66.90	68.80
CH_4	38.45	39.60	41.30	42.00	39.60	37.40	27.00	20.70	18.60
C_2H_6	3.00	2.70	1.70	1.30	....	....	....	....	....
CO_2	1.95	2.85	2.40	2.20	1.95	2.50	1.80	1.90	2.70
O_2	.40	.20	.20	.15	.55	.20	.30	.30	.80
N_2	1.00	1.65	1.50	1.15	2.60	1.90	2.00	1.80	2.50

A standard gas coal should produce from 3000 to 3400 B.T.U. per pound (B.T.U. x yield); this is somewhat affected by the type of carbonizing apparatus used, the verticals and through horizontals giving the highest results, while coke ovens give somewhat lower figures.

Minor Gas Constituents. In addition to the other gases which have been considered, ammonia, cyanogen, hydrogen sulfide, naphthalene, carbon disulfide and traces of some other organic sulfur compounds that need not be considered are present. The ammonia and hydrogen sulfide both appear early in the distillation, soon reach their maximum and then decline, the ammonia somewhat faster than the hydrogen sulfide. The cyanogen and carbon disulfide on the other hand gradually increase as the temperature rises.

Ammonia and Cyanogen. There seems to be some connection between the proportion of ammonia and cyanogen which has been explained by the probable reaction



$$NH_3 \begin{cases} 2CN + 3H_2 \\ N_2 + 3H_2 \end{cases}$$

The critical temperatures of maximum yield seem to be about 850° to 900° F. for ammonia and from 1650° to 1750° F. for cyanogen. When the temperature rises above 1800° F., these gases seem to be decomposed into their elements.

The yield of ammonia and cyanogen is naturally dependent upon the amount of nitrogen present in the coal, but is apparently more affected by the system of carbonization. Generally, with the higher temperatures, the yield of ammonia is decreased while the cyanogen increases, but this is not always the case, the ammonia and cyanogen sometimes varying in the same direction. It will be noted from Table 10 that the horizontal retorts yield less ammonia than either the vertical retorts or the coke ovens.

TABLE 10—TYPE OF RETORT AND AMMONIA YIELD

	Horizontal	*Vertical*	*Coke Ovens*
Nitrogen in Coal	1.25%	1.31%	1.29%
Ammonia, as NH_3 per ton	4.5#	6.1#	6.8#
Cyanogen, as CN per ton	2.4#	1.2#	1.5#

Sulfur Compounds. The ratio and quantity of hydrogen sulfide and carbon disulfide seem to vary not only with the temperature but also with the method of carbonization as the vertical retorts apparently yield less fixed sulfur compounds than the horizontal retorts and probably more hydrogen sulfide. In general the total sulfur compounds in the gas increase with the sulfur in the coal, but a table below shows how the sulfur is distributed with some American coals when tested in horizontal retorts.

TABLE 11—RELATION OF SULFUR IN COAL AND COKE TO HYDROGEN SULFIDE AND SULFUR COMPOUNDS

Coal	*Sulfur in Coal*	*Sulfur in Coke*	*Grains per 100 Cu. Ft.*	
			Hydrogen Sulfide in Gas	*Sulfur Compounds*
Equality	6.76%	2.27%	2190	45.51
Marian	2.39	2.38	955	30.00
Montana	1.64	1.53	735	45.30
Cartersville	1.59	1.28	910	40.45
Gaston	1.35	1.15	702	65.23
Big Muddy	1.21	.82	340	17.42
Youghiogheny	1.01	.93	420	17.28
Farmington	.96	.84	400	18.64
McAllister	.94	.66	260	12.00

Naphthalene **is an impurity that may give rise to great trouble in the distribution system if not removed from the gas. While small amounts may be formed at relatively low temperatures the excessive formation is due to high temperatures in the retort.**

Vertical retorts form very little naphthalene, averaging about 2 lbs. per ton; coke ovens will give about 6 lbs., while horizontal retorts at high temperatures may give over 11 lbs. per ton of coal.

The conditions governing the formation are such that, except for the choice of apparatus, efficient operation must result in the formation of some naphthalene that must be removed by proper treatment.

Nitric Oxide. A trace constituent in the gas that has given rise to a great deal of difficulty in the distribution system is nitric oxide. While it has been argued that nitric oxide may be formed in the carbonization of coke, it is now generally believed that its presence in coal gas is due primarily to products of combustion being drawn into the gas through leaks in the walls of the carbonizing vessels. If this gas, which may exist in concentrations as low as one part in ten million, is not removed from the plant, it will spontaneously oxidize to NO_2 and combine with many of the hydrocarbon vapors in the formation of certain microscopic particles of a resinous material that remains dispersed in the gas and which has received the name of "vapor phase gum." This material is carried through a distribution system and is deposited at points where the gas passes through minute openings, such as the adjusting needles in range and hot-water heater pilots and the regulating valves in gas-operated refrigerators. This phenomenon has only been noticed as the result of the very extensive use of gas-burning appliances provided with automatic control devices in which the gas is wire-drawn through very small orifices or passages. The formation of this type of gum probably always occurs even when the appliance design is such that its presence does not result in stoppages.

TABLE 12—COMPOSITION OF VARIOUS TYPES OF TARS

	Low Temperature	*Continuous Verticals*	*Intermittent Verticals*	*Horizontal Retorts*	*Coke Ovens*
Specific gravity 25° C.	1.07	1.15	1.08	1.25	1.18
Free carbon	0.7%	12.0%	3.8%	24.0%	5.7%
Tar acids	13.7%	6.8	10.3	2.5	1.5
Sulfonation residue	17.5%	3.2	2.6	0.8	0.3
Coke	21.0%	31.0	20.0	46.0	21.0
Naphthalene	None	0.09	0.03	0.32	0.71
Distillation:					
Oil to 210° C.	15%	2%	6%	1%	1%
Oil to 235° C.	20	7	15	6	10
Oil to 270° C.	33	15	28	12	20
Oil to 315° C.	50	22	36	18	29
Oil to 355° C.	65	33	50	29	40

Coal Tar. In addition to the gaseous hydrocarbons formed during the third stage of the carbonization, the very complex mixture of ring hydrocarbons and their derivatives having boiling points considerably above that of water are formed and condensed into what is known as tar. Table 12 gives a comparison of the distillation of a number of samples from the different methods of carbonization.

This shows the variation in the character of the hydrocarbons that are formed with the increasing time of distillation and increase in temperature. The increasing gravity and the higher fixed carbon content denote the increasing complexity of the hydrocarbons formed.

The yield of tar varies with the coal and other carbonizing conditions. It generally decreases with higher temperatures and an increased yield of gas.

With the low-temperature processes the yield of tar may reach 23 gals. per ton; with vertical retorts, from 12 to 15 gals.; horizontal retorts, 9 to 13 gals., while from coke ovens it will be from 6 to 9 gals.

Coke. The character and amount of coke or the carbonaceous residue that remains in the retorts after the distillation is dependent upon the coal used, the process of carbonization, and the temperatures employed.

TABLE 13—COMPARATIVE COKE ANALYSES

	Bee-Hive Ovens	*Retort Coke Ovens*	*Vertical Retort*	*Horizontal Retort*
Moisture	.35	1.25	1.35	2.57
Volatile compounds	.34	1.61	1.73	3.84
Fixed carbon	92.69	86.66	87.40	86.05
Ash	5.89	10.48	9.52	7.54
Sulfur	.74	.77	.99	.96
Real gravity	1.83	1.90	1.82	1.73
Per cent of coke	52.07	49.49	59.25	53.89
Per cent of cells	47.93	50.51	40.75	46.11

The cause of the coking tendency of coke has been extensively studied and appears to be related to the presence of the so-called "resinic" component as determined by solvents. Generally, coals containing more than 10 per cent of oxygens seem deficient in coking properties.

A great deal of study has been given to the admixture of different coals in order to produce better grades of coke.

Most coke-oven plants use a mixture of high volatile and low volatile coals in order to produce cokes having the desired qualities for the particular market available. For domestic coke, ready ignition and freedom from dust are important considerations, while for blast furnace purposes the ability to stand crushing and abrasion is important. The coke produced from some coals is improved by the addition of a small quantity of coke breeze.

The character of the coke is also affected by the rapidity of the carbonization.

In ordinary retorts where coals high in volatile matter are used and the time is short, say, 4 to 5 hours, the coke is quite soft and porous. As the time of carbonization increases and the charge is enlarged the coke becomes denser and harder and more metallic in appearance. In the coke oven where the coking time may extend to 18 to 24 hours the coke becomes suitable for foundry and blast furnace purposes.

In some of the metallurgical applications the size of the coke is of importance and this is determined by the size of the charge in the carbonizing vessel, as the coke on cooling develops radial crocks outward from the center so that the "fingers" will be approximately half the smallest dimensions of the charge.

The percentage of fixed carbon in the coal practically fixes the percentage of coke yield, yet this is affected slightly by the system of carbonizing, the vertical retorts yielding a slightly higher percentage than the horizontal retorts while with the coke ovens there is a considerable increase; in this case, however, the increased yield of coke seems to be at the expense of the tar.

Table 13 of analyses of the coke from the different processes shows clearly the above variation in physical characteristics.

CARBONIZING EQUIPMENT

We have pointed out that the more important method of coal carbonization, from a volume standpoint, is the coke oven, but there are still in existence large numbers of what are known as horizontal retorts, especially in the smaller plants. The operation of this type of carbonizing equipment will be briefly described.

Horizontal Retorts—Figure 2 is a sectional elevation of a bench of through "nines."

The retorts in the stop-end bench are of fire-clay or silica, 9 ft. long of D section, 16 by 26 in. and are 3 in. thick; in the through bench, the retorts are 20 ft. long. The retorts are provided with an iron mouthpiece with a self-sealing door operated by a system of eccentric cams and levers. It will be noted that the stop-end retorts have only one mouthpiece while the "throughs" have two, one at each end. From the mouthpiece the gas passes up through what is known as an ascension pipe to the bridge pipe and thence down through the dip pipe into the hydraulic main.

When the benches are operated at very high temperatures to secure the maximum yield of gas, and especially with certain coals, the ascension bridge and dip pipes became choked with a hard carbonaceous deposit that is sometimes very difficult to remove. Removable covers are provided so that cleaning tools may be used to remove these deposits. Many schemes have been devised to remedy this difficulty. One consists in arranging three retorts in a vertical plane and using a single straight ascension, or as it is frequently called, stand pipe; this is then cleaned with a mechanically-driven auger. Another device connects the retorts by a side connection with a large rectangular stand pipe provided with internal slide valves for each retort, down which a stream of water or weak ammoniacal liquor is constantly circulated, which is removed by a sealed overflow tank at the bottom. This latter device appears to eliminate entirely all difficulty from stoppage.

The Hydraulic Main. The hydraulic main is now usually made of steel plate, and is either round or "D" shaped and is filled to a fixed level with ammoniacal liquor so that the end of the dip pipes are sealed by the liquor, thus preventing the escape of the gas while the retort is being charged, and at the same time allowing the gas to enter freely the hydraulic main.

In the older installations the hydraulic main was usually continuous, run-

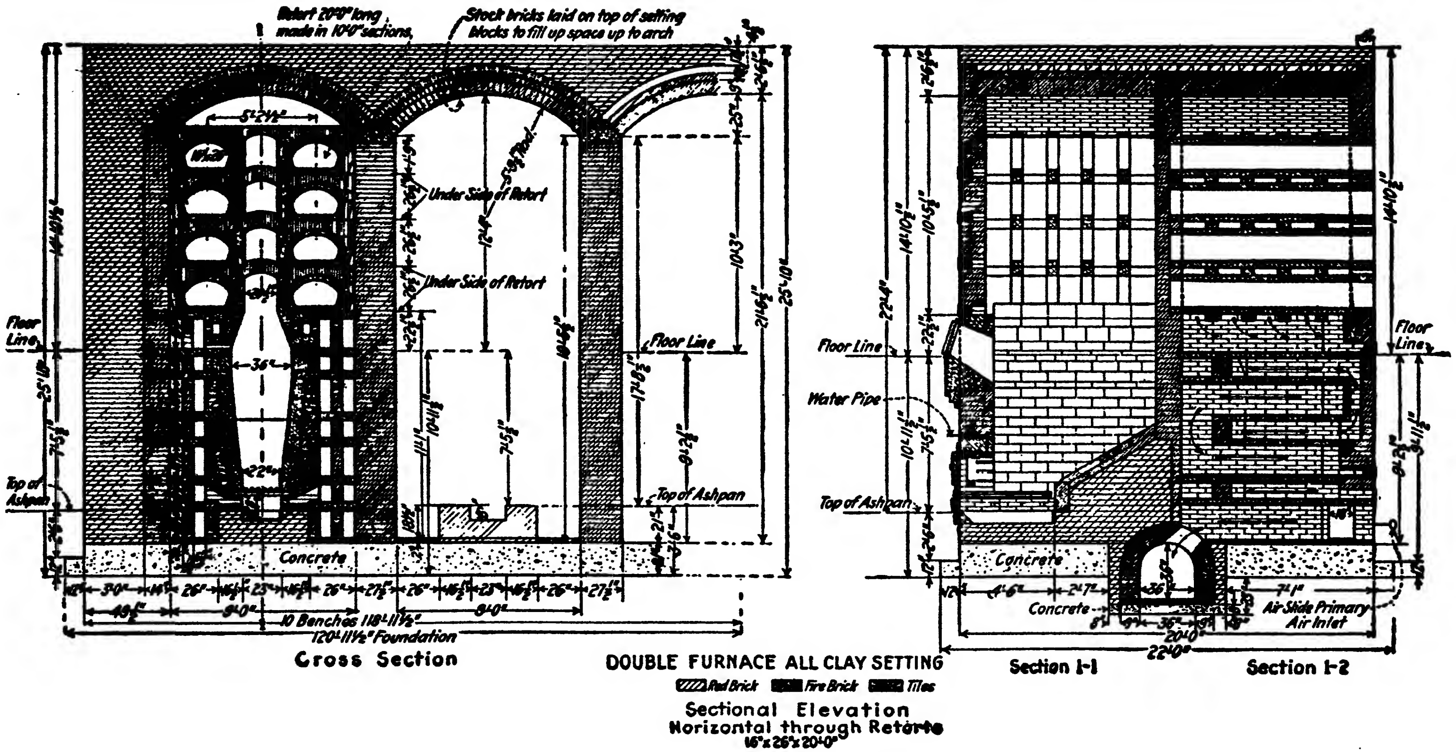


FIG. 2. Horizontal Retorts.

ning the entire length of the stack. This arrangement frequently gave trouble, due to uneven settling of the bench construction throwing it out of level. In the later construction each bench has an individual small main.

In many later plants an automatic device is used whereby the level of the liquor in the hydraulic main may be raised, thus sealing the dip pipes when the retorts are to be charged, or put out of service for any reason. Then by pulling a lever the level is dropped below the dip pipes, thus putting the retorts in direct connection with the discharge pipes and eliminating the vibration set up by the passage of the gas through the water seal.

Mechanical devices are also used for agitating the tar in the bottom of the hydraulic main. This prevents the formation of pitchy deposits which are difficult to remove and which would in time seriously obstruct the operation of the main.

From the hydraulic main the gas passes by means of a large pipe called the "foul main" to the condensing and purifying apparatus, which will be taken up later.

The Gas Producer. Gas for heating the coal is provided by a gas producer.[8] The producer is provided with grate bars and cleaning doors and is charged with hot coke as it is drawn from the retorts through the charging door on the upper floor level. The primary air enters through regulating shutters at the front of the bench, passes around the lower waste gas flues and hence beneath the grate. Rising through the fuel it combines with the carbon, forming producer gas. Steam is admitted beneath the grate to soften the clinkers and control their formation by lowering the temperature of the fuel bed. This is due to the endothermic nature of the reaction with the carbon of the fuel.

Heating the Retorts. As the producer gas rises through the *nostrils* into the *combustion chamber* it meets the secondary air which is admitted through regulating shutters below and at the front of the bench. The air travels through fire-brick ducts in what is known as the *recuperator,* where it passes horizontally to the right and left and upward and is heated by the waste gases to a temperature of from 1600° F. to 1800° F., practically attaining the temperature of the waste gases.

As the combustion takes place the hot products of combustion rise around the retorts to the top of the combustion chamber and are then drawn down and toward the front of the bench, where they enter the waste gas flues in the recuperator, passing horizontally front and back and downwards, giving up their heat to the incoming secondary and primary air. The waste gases finally pass to the back of the bench and hence to the stack, the draft of which is controlled with a damper set at a convenient point in the recuperator.

The temperature in the bench is regulated by a proper admission of primary air to the recuperator and by adjusting the secondary air supply so that a slight excess of oxygen is present in the waste gases (about 1.0 per cent). The distribution of the heat is controlled by the stack draft which is usually so regulated that the pressure in the furnace is just at a balance. In the combustion chamber the temperatures may vary from 2600° F. to 3200° F., just above the nostrils, to from 1900° F. to 2200° F. at the entrance to the recu-

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[8] See Chapter 19.

perators. Where the products of combustion are used under the grate instead of steam these temperatures will be several hundred degrees lower. In the retorts the temperature will vary from 1600° F. to 1800° F.

Modifications of Retorts. In the older plants the coal was charged into the retorts with shovels by hand and the coke withdrawn with iron rakes, but in the larger plants mechanical charging and discharging machines are used.

Various modifications of the horizontal retort have been tried in the industry, primarily with a view to reducing the labor and expense of charging the coal and removing the coke. In one modification the retorts are set at an angle of about 32 degrees to the horizontal. These retorts are called "inclined retorts." The coal is fed in at the top by gravity and when fully carbonized the coke slides out at the bottom.

Following this, the retorts were made vertical, as this should theoretically result in a larger yield of gas per square foot of ground area.

Vertical Retorts—A further improvement, with a view to increasing the production of gas, was the development of the continuous vertical retort in which the coal is continuously fed into the top of the retort and the coke is continuously removed from the bottom. (Figure 3 shows one form of the continuous vertical retort that has been used in the United States.)

A modification of the intermittent vertical retort is known as the "vertical oven" and this is essentially an enlarged vertical retort that is charged through charging holes at the top and provided with a long, narrow door for discharging the coke. (Figure 4 is an installation of one type of vertical oven that has given very satisfactory results.) These ovens hold two tons of coal and are usually arranged with three ovens in a batch.

It will be noted that all of these forms are heated by producer gas, generated either in producers built as an integral part of the bench or in separate plants. The proper and efficient operation of a producer and the maintaining of a uniform and effective temperature in the carbonizing chambers are the important factors in successful bench operation.

The advances that have been made in recent years in the efficiency of many of our manufacturing processes are based on the great advance in our knowledge of the mechanism of combustion, and in the refinements and methods for its accurate control.

The important factors in the operation of the producer are proper regulation of the drafts and the admission at a uniform rate of the requisite quantities of primary and secondary air required in order that a suitable temperature may be maintained. To insure the efficiency of this combustion the flue gases must contain a high percentage of carbon dioxide. Accurate commercial instruments are now available for the determination and the control of all of these factors.

The use of external producers has resulted in considerable saving of labor and more uniform bench operation and in a considerable saving in fuel due to the fact that unsalable sizes of coke can be used as fuel.

Figure 4 shows the installation of an external producer. The producer is fed mechanically from fuel stored in the overhead bin. The ashes are removed continuously from the bottom and fall into a hopper for removal

The steam and air are metered and the gas analysis is recorded automatically. A large dust catcher is provided for cleaning the gas before it goes to the benches.

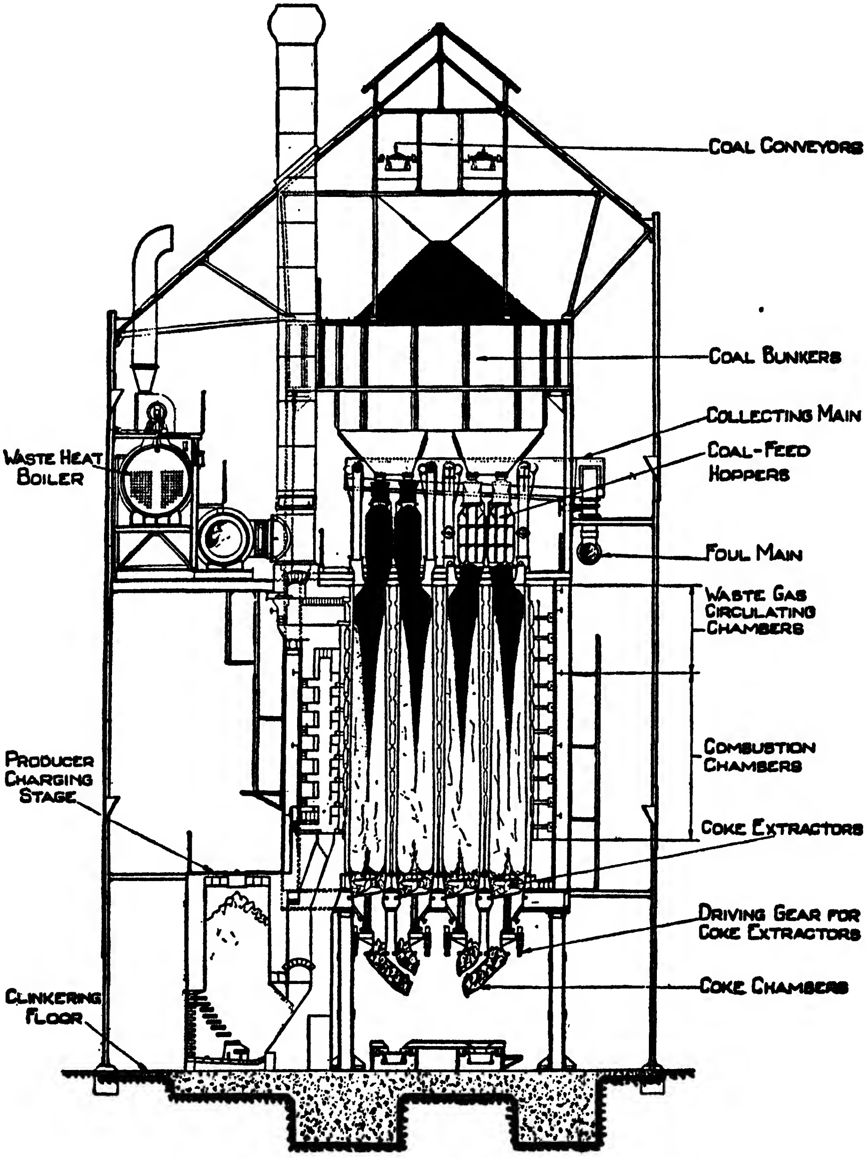

Fig. 3. Glover-West Continuous Retorts. (Courtesy West Gas Improvement Co.)

While the use of external producers has not reduced very greatly the actual pounds of fuel used per ton of coal carbonized, in the case of the individual producers this was generally the hot coke as drawn from the retorts while the external producers have used cold coke, breeze, and other unsalable coke sizes, thus greatly increasing the pounds of salable coke per ton of coal carbonized.

Modern individual producers will usually require from 300 to 350 lbs. per ton of hot coke, while external producers will operate on less than 300 lbs. per ton of coke and breeze.

Since the fuel and ash are handled automatically, labor is reduced to inspection and the uniform quality of gas produced results in very efficient heating of the benches which is reflected in their increased capacity and perfectly uniform and regular operation. Waste-heat boilers are connected between the bench and the stack. In a plant of 2,000,000 cu. ft. capacity such waste heat boilers will generate about 150 B.H.P.

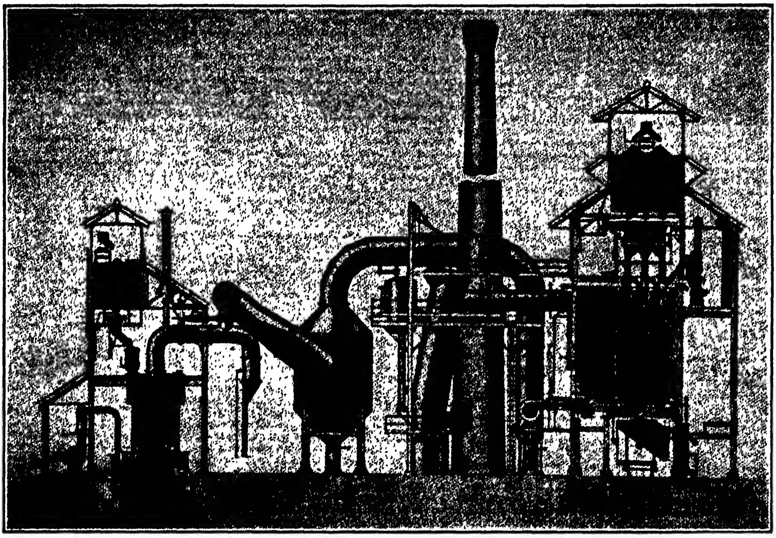

FIG. 4. The U. G. I. Intermittent Vertical Retort System with Detached Producer and Waste Heat Boiler.

By-Product Coke Ovens—The general tendency has been, therefore, toward the use of larger carbonizing units and this has resulted in the extensive use of the by-product coke oven, which was developed primarily to produce metallurgical coke for use in the manufacture of iron and steel. Figure 5 shows a cross-section of the type of coke oven known as the "Becker Oven" manufactured by the Koppers Company. The oven proper is a narrow rectangular chamber built of silica brick, from 10 to 13 ft. high, about 30 ft. long, with the width varying from 14 to 17 in., being wider at the discharge end of the oven.

The method of heating is different from that described under the horizontal retorts in that the waste heat is recovered and utilized in regenerators,[4] i.e., chambers filled with fire brick which alternately absorb the sensible heat from the offgoing products of combustion and give it up to the incoming secondary air so that operations are intermittent instead of continuous, as in the previ-

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[4] See also Chapter 23.

ously described recuperators. In the type of oven illustrated, the heating gas, which may be coal gas itself, producer gas, or even blast furnace gas, is introduced through regulated jets and meets the secondary air which has been preheated in passing up through the regenerators. Combustion takes place in a number of vertical flues along the length of the oven, products of combustion passing up on one side of the oven through cross-over flues, down on the other side of the oven, thence out through the regenerators, where their sensible heat is recovered, and then into the stack. It may be noted that there are two sets of regenerators to each chamber so that they work alternately, absorbing and giving up their heat.

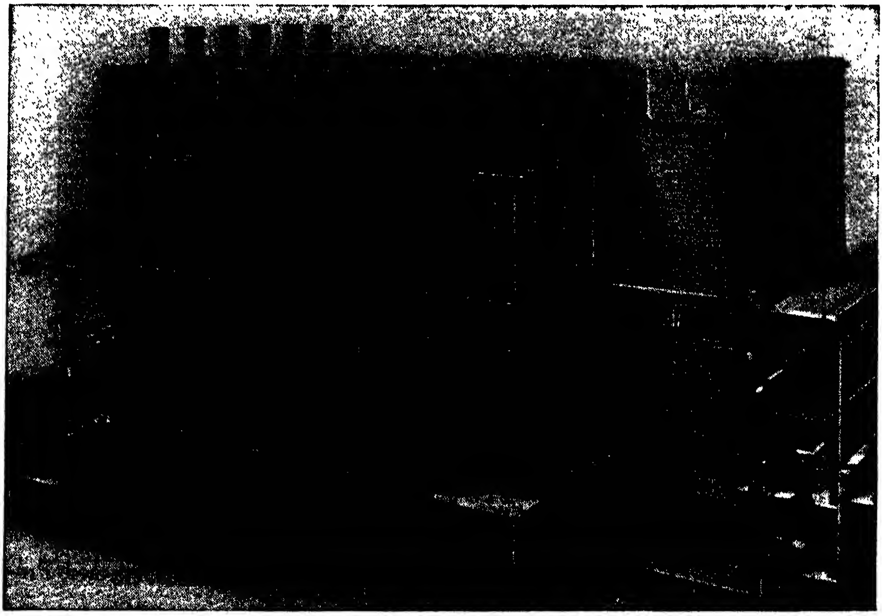

Fig. 5. Cross Section of Becker Oven as Manufactured by the Koppers Co.

The ovens are filled by charging holes in the top and the end openings are closed with self-sealing doors. The gas produced is collected in hydraulic mains in the same general fashion as in the horizontal retorts. At the end of the coking period the doors are removed and a mechanically-operated ram pushes the coke out of the retort into cars in which it is quenched in a quenching tower, usually somewhat removed from the oven proper to avoid the nuisance of smoke and dust.

The size of the ovens can be varied to hold from 4 or 5 tons up to as high as 20 tons. (Figure 1 shows the complete by-product coke-oven plant in which the gas produced is distributed in a large Eastern City.)

In the original by-product coke-oven operation, the so-called lean gas, or that produced during the latter part of the carbonizing period, is used for heating the ovens. Where the maximum yield of gas is desired the coke ovens are now being fired with external producers utilizing small coke and breeze for fuel, thus permitting all the gas made to be available for sale and utilizing the unsalable coke sizes.

Products of Different Carbonizing Systems—We may summarize the principal operating results from different types of carbonizing systems in Table 14.

TABLE 14—PRODUCTS OF DIFFERENT CARBONIZING SYSTEMS

System	*Horizontal Retorts*	*Intermittent Verticals*	*Continuous Verticals*	*Coke Ovens*
B.T.U. in gas for sale per pound of coal.	3265	3320	3300	1820
B.T.U. required for heating per lb. of coal	1920 (coke)	1900 (coke)	2560 (coke)	1290 (gas)
Tar yield gallons per net ton	12.2	14.2	12.6	8.3
Ammonia as sulfate pounds per ton	17.0	24.4	18.4	24.0
Coke for sale, pounds per ton	1000	1005	900	1360

LOW TEMPERATURE CARBONIZATION

At the lower carbonizing temperatures, say below 600° C., production of tar is over twice that at the usual operating temperatures of 1000° C. The coke formed at these low temperatures is quite different from the high temperature coke in that it is somewhat softer and has a relatively low temperature of ignition. These factors have suggested the idea of carbonizing coal at low temperatures to make a smokeless domestic fuel and to secure a high yield of tar as a by-product. Many processes have been tried, but in general they have not been successful in commercial operation.

Recently there has been introduced a process which carbonizes the coal in a thin layer in an oven heated only at the bottom. This is known as the "Curran Knowles process" and is essentially a coke oven laid horizontally and heated only from the bottom. The yield of tar is said to be higher than that produced in ordinary coke ovens, the yield of gas is lower, and the coke is considerably softer but is claimed to be satisfactory for domestic purposes.

Due to the fact that both the coke and oils that are produced are different from the products of high temperature distillation, it is difficult to predict the commercial success of these processes until time has determined whether they should be considered from the viewpoint of having coke as a main product and the gas and oil as by-products, or whether the oil should be considered the main product.

Mechanical Coal and Coke Handling Devices—In the smaller plants the coal and coke were usually handled manually in iron wagons known as "buggies," but with the increase in the size of the more modern plants mechanical methods soon became imperative, not only on account of the difficulty and increased cost of obtaining the necessary labor, but also because of the enormous quantities of material to be handled, so that in the modern plants the coal and coke are handled entirely by machinery, and almost automatically.

Locomotive cranes are frequently used for unloading from cars.

In handling coal from the crushers into the charging bins, belts or bucket conveyors are used, the belt type being preferred where the space is available.

The long belt conveyors which are used for handling the coal and the coke are shown quite clearly in Figure 1.

The hot coke from the retorts is now generally handled by mechanically-operated cars running on rails beneath the retorts, or by cars on the discharge side in the case of the Koppers ovens. After the hot coke has been quenched it is usually crushed and screened into several sizes and the breeze removed. The skip type of conveyors is frequently employed for handling coke and ashes.

HANDLING THE VAPORIZED PRODUCTS

As the crude coal gas leaves the retorts and is brought into contact with the liquid in the hydraulic main, it deposits a portion of the higher boiling hydrocarbon vapors as tar and some of the ammonia is absorbed. Due to the fall in temperature the gas becomes partially saturated with water-vapor; tests indicate from 60 to 95 per cent saturation.

The crude gas leaves the hydraulic main at a temperature of from 130° to 150° F., and contains a number of impurities—tar, ammonia, sulfureted hydrogen, organic sulfur compounds, naphthalene and cyanogen—which must be removed in whole or in part before the gas is considered ready for distribution, and furthermore, the gas must be brought down to the ordinary temperature. The average content of the impurities in the crude coal gas is given in Table 15.

TABLE 15—IMPURITIES IN CRUDE COAL GAS

Impurity	*Percentage by Volume*	*Grains per 100 Cu. Ft.*
Hydrogen sulfide	.4 -1.6	250–1000 sometimes 3000
Ammonia	.48 -1.26	150–400 occasionally 550
Cyanogen	.05 - .135	25–65
Organic sulfur	.0085- .046	12–65
Naphthalene	.084 - .210	200–500
Nitric oxide	....	0.015–0.3

Condensers—When the gas leaves the hydraulic main it contains, in addition to the impurities just mentioned, a very complex mixture of hydrocarbons of widely varying boiling points, and the water vapor with which it is partially saturated. Some of the hydrocarbons are fixed gases at the ordinary temperatures while the others may be vapors, liquids, or solids; practically all are mutually soluble and, to some extent, in water. The essential object to be attained in condensers is the removal of those vapors which might otherwise be condensed and collect in the distribution system. The principal constituents to be removed are the tar, naphthalene, and water vapor together with certain of the higher boiling hydrocarbons, such as styrene and indene.

The work to be done in condensation is primarily the removal of the latent and sensible heat of the water vapor carried by the crude gas, the sensible heat of the tar and the gas itself being very small.

If the gas left the hydraulic main at 140° F. saturated with water the total heat above 60° F. would be about 16,300 B.T.U. per M. measured at 60°, made up as follows:

	B.T.U.
Gas	1,600
Tar	1,700
Water	13,000

The importance of the percentage saturation of the gas is evident. If it could be reduced to 60 per cent, there would be 32 per cent less heat to be removed in the condensers.

In addition to removing the tar it is very desirable to remove as much of the naphthalene as possible during the condensation. This takes place principally by the solution of the naphthalene in the condensing tar vapors and fog and while there is theoretically sufficient tar to take up all but a negligible amount of naphthalene, the time factor is apparently too short to permit the naphthalene in the gas to come into equilibrium with the tar so that only a portion of the naphthalene is removed.

Opinion is divided as to the best system of securing the most efficient results. One system makes use of tubular condensers arranged to secure high velocities of both gas and water to drop the temperature and then completes the removal of the tar by tar extractors of the P. & A. or static type. The other system lowers the temperature and removes the tar and some of the ammonia by intensively scrubbing the crude gas with ammonia liquor that is sprayed in relatively large quantities against a rising stream of gas in grid-filled towers. The hot liquor is cooled in cooling coils with water or with refrigerating coils. The tar is removed as it collects and the liquor returned to the system, which is a closed one, to prevent loss of ammonia. Small traces of tar are removed by a washer scrubber and the ammonia is removed by countercurrent washing with water in a system of four or five towers.

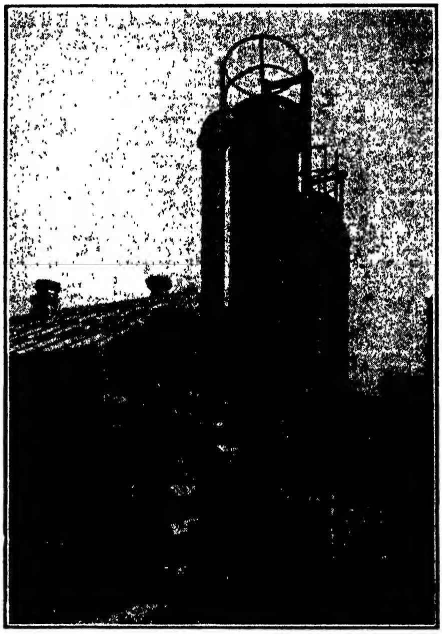

FIG. 6. Scrubber Condensers. The gas is cooled by direct contact with cooled water or ammonia liquor.

Types of Condensers. The tubular condensers used in the first system are now being so designed that very high velocities are secured both of the gas and water; some of these are arranged so that the gas makes four passes in one shell. Figure 7 is a type with a double pass.

In the scrubber condenser system (Figure 6) the condenser consists of one or more towers relatively narrow and high and packed with wooden grids, ½ in. by 6 in. deep spaced ½ in. apart. In this way a relatively large surface covered with the cooling liquor is exposed to the gas and the gas velocities can be greatly increased, thus very greatly improving the efficiency of the apparatus.

Tar Extractors—Some tar usually remains in the gas after the condensers and this is removed with some form of tar extractors.

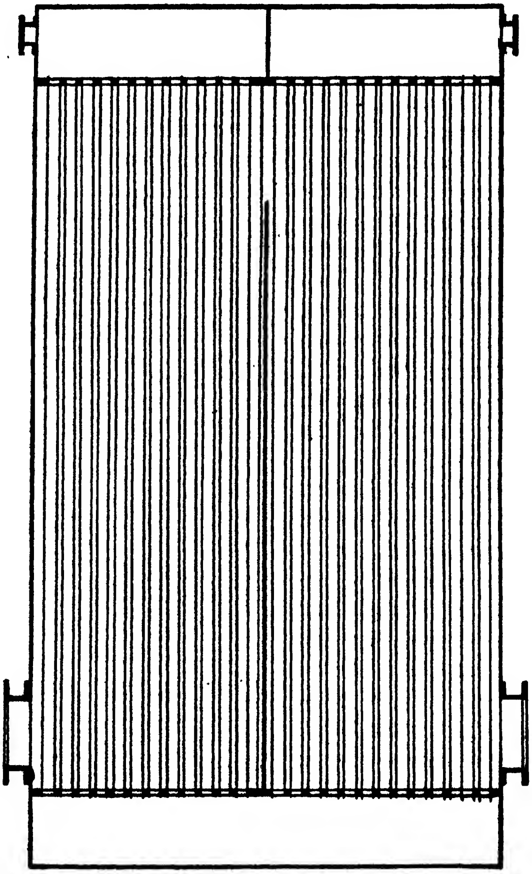

FIG. 7. Two-pass Water Tube Condenser.

The early form of tar extractors was usually of the P. & A. type (Figure 8), which consists of a drum composed of a series of perforated sheets consisting of alternate series of small holes and blanks so arranged that the blank spaces in one set of sheets opposes the perforated sections in the adjoining sheets. Another form of apparatus (Figure 9), is known as the washer scrubber. In this, the gas passes through a number of small openings into contact with ammonia liquor, the action of the water causing the tar particles to coalesce and be condensed.

The Cottrell Precipitator. The more modern apparatus for the removal of mist which may be composed of tar, hydrocarbon, water vapor, or even solid material in the form of dust, is of the electrostatic type known generally as the Cottrell Precipitator. (Figure 10 shows one form of this apparatus.) In general it consists of a vessel containing a number of tubes 3 or 4 inches in diameter through which the gases pass in a downward direction. In the center of each one of the tubes a wire is suspended by suitable insulators at the top and with weights so that it will remain accurately in the center of the tube. This wire is charged with a direct voltage usually from 50,000 to 70,000 volts, produced by a mechanical rectifier operating from a synchronous motor. A rather elaborate mechanical construction is required in order to prevent breakdown of the insulators due to the deposition of a film of moisture from the crude gas. Because of the high voltage the particles are ionized and then under the influence of the strong electric field are given velocities which are sufficient to cause them to impinge upon the inner surface of the tubes. Smaller particles then coalesce and are withdrawn from the precipitator proper through a seal. When properly operated these precipitators will remove from 95 to 99 per cent of the suspended material.

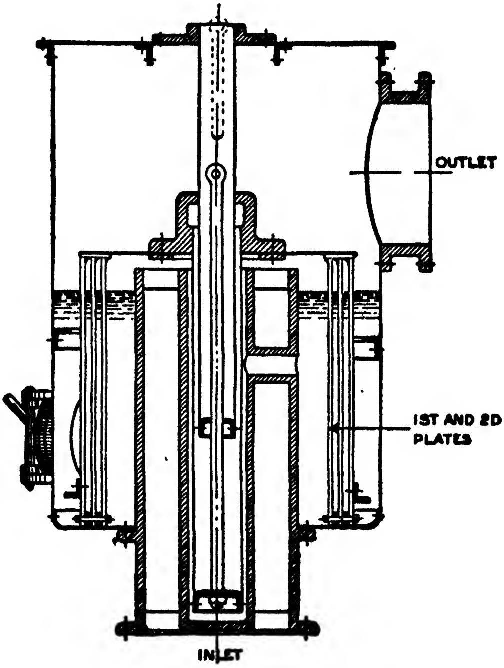

Fig. 8. P. & A. Tar Extractor.

Exhauster—The position of the exhauster is varied somewhat in different arrangements of the purifying systems, but is generally located after the condensers, to take advantage of the smaller volume of gas to be handled, and before the scrubbers.

The function of the exhauster is to maintain a uniform pressure on the retorts by removing the gas as fast as it is generated.

The positive displacement type of exhauster is shown in Figure 11, while in Figure 12 is shown the centrifugal type. One advantage of the centrifugal type of exhauster is the fact that it will remove small traces of tar.

As the make of gas varies from minute to minute various forms of governors are employed to maintain uniform pressure conditions.

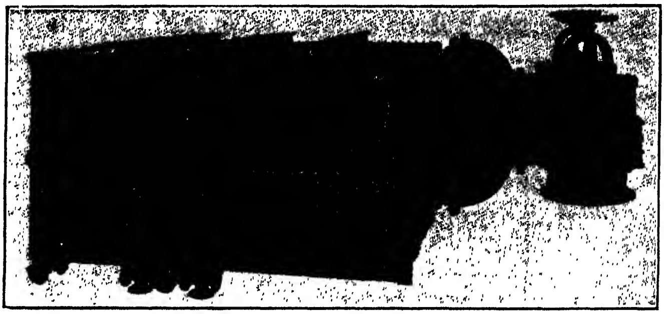

Fig. 9. Washer Scrubber.

The governor may vary the power supply to the exhauster, operate on a by-pass, or in some installations the governor may be located at the retort house and varies the opening to the foul main.

In the by-product coke ovens, due to the very large number of joints in the oven walls, the maintenance of closely controlled pressures in the oven is of very great importance.

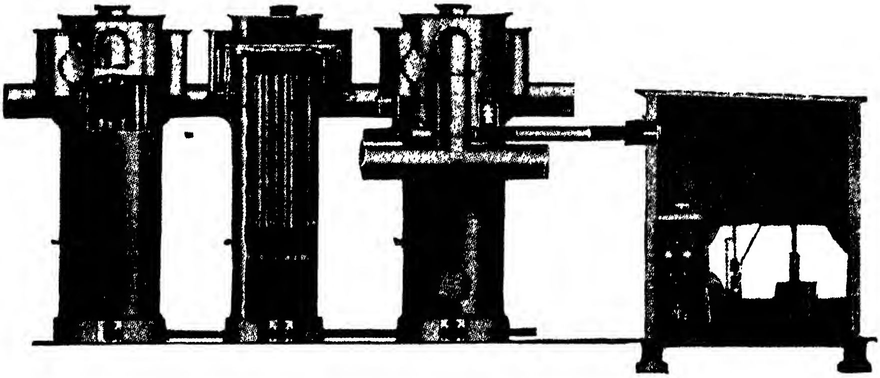

Fig. 10. Cottrell Electrical Tar Precipitator.

Scrubbers—From the exhauster the gas passes into the one or more of a series of scrubbers for the removal of naphthalene, cyanogen, and ammonia. Four general types are in use: tower, static, rotary, and centrifugal.

The tower scrubber was the original form and consists of one or more steel towers filled with various materials to break up the upward stream of gas and to increase the surface covered with the scrubbing liquid that is sprayed in at the top and passes downward by gravity. Coke, quartz, various forms of wooden trays, boards set on edge, etc., have been used for this purpose. This type of scrubber is the least efficient considering its cubical capacity but is fairly efficient if built quite high per square foot of ground space required.

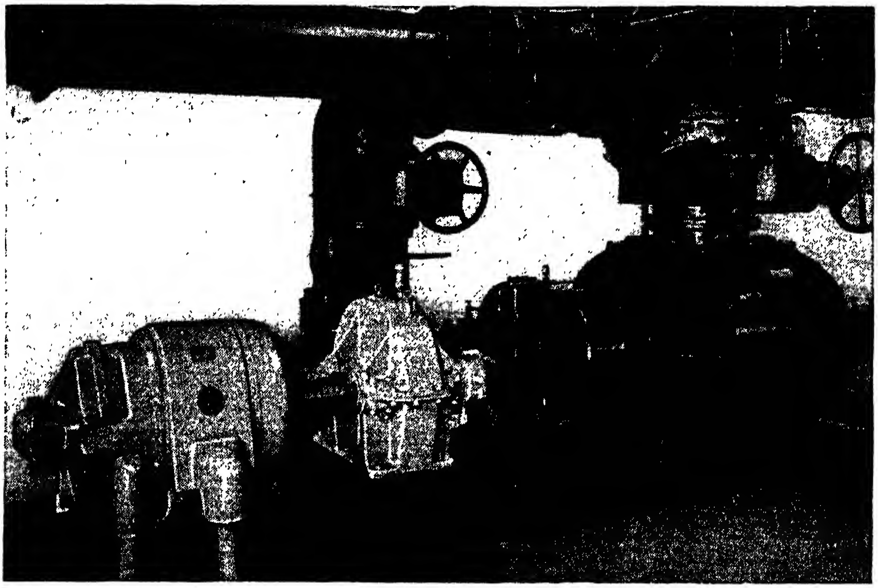

FIG. 11. Positive Gas Exhauster.

Various forms of ceramic tile have been developed which will give a much higher ratio of wetted surface to cubical contents together with a lower resistance. This type of tower filling, when properly operated, will give efficient results. In the static type the gas is forced to pass in contact and bubble through the scrubbing liquid by a series of partitions arranged across the flow

FIG. 12. Centrifugal Exhauster.

of gas in a rectangular containing vessel. Another series of divisions permits the level of the scrubbing liquid to be regulated in the various compartments thus formed so that the most efficient depth of seal may be maintained.

The increased efficiency of the tower type of scrubber that has been obtained with a better comprehension of the design requirements has very largely eliminated the more expensive rotary and centrifugal types of scrubbers formerly in use.

Removal of Ammonia—In the smaller gas plants the ammonia is generally removed by scrubbing with water in some form of tower scrubber. Usually one or more towers are used. In the first tower in the series a weak ammonia solution is circulated by centrifugal pumps so that its strength is built up from 1 to 1½ per cent of ammonia. In the final tower fresh water is used so that the ammonia is reduced to less than one grain per hundred cubic feet. This will require from 10 to 15 gallons of fresh water per ton of coal. Due to the constant recirculation of the ammonia liquor there is some removal of hydrogen sulfide and carbon dioxide in this stage of the process.

In the coke-oven plants the ammonia is usually recovered as ammonium sulfate by scrubbing the gas with a weak solution of sulfuric acid.

A number of processes have been invented for the extraction of the ammonia from the heated gasses and the direct formation of ammonium sulfate; among these are the Otto, Collin, Koppers, and Feld.

In the Koppers system, the gas is separated from ammonia liquors as it enters the collection main from the oven. The crude gas is then cooled in the primary cooler where the tar and most of the ammonia are condensed and washed out. Gas is then drawn by the exhauster through the tar extractors where the remaining tar is removed. The gas is then reheated and is forced through the saturators where it comes in contact with a dilute solution of sulfuric acid, forming ammonium sulfate that is precipitated as a solid salt. It is necessary to reheat the gas so that it will be able to carry off the water formed in the reaction between the sulfuric acid and the ammonia to prevent the accumulation of excess liquid in the saturator. The sulfate formed in the saturator is dried in a centrifugal dryer.

The ammonia in the liquor which is collected at various points, principally at the primary coolers, is pumped to a storage tank and is driven off in stills. The ammonia vapor thus recovered is added to the gas just before the saturators.

After leaving the saturators the gas is passed to a final cooler where it is frequently washed with water and in some cases it passes to a naphthalene scrubber in order to control the amount of naphthalene remaining in the gas.

Removal of Naphthalene—Final naphthalene removal is effected by scrubbing the gas with oil. The object to be attained is the maximum removal with minimum expense of scrubbing oil. This is usually obtained in the tower type of scrubber by combining the rapid recirculation of a relatively large amount of scrubbing oil through the lower portion of the tower and the use of fresh oil in relatively small quantities in the upper portion of the tower.

The fresh oil is fed intermittently by a device so arranged that a sufficient quantity of oil is suddenly released so that all of the wetted surface is thoroughly flushed with a fresh film.

Separation of Tar—The ammonia liquor and tar that are removed in the different points in the condensing and purifying system are collected and passed through what is known as a separator. In this apparatus, the stream of mixed liquor in passing through the separator is baffled and turned in its course a number of times, so that the tar which has a specific gravity of 1.2, and higher, falls to the bottom and may be removed, while the liquor rises to the top and may be pumped off to the ammonia storage tanks. (See Figure 13.)

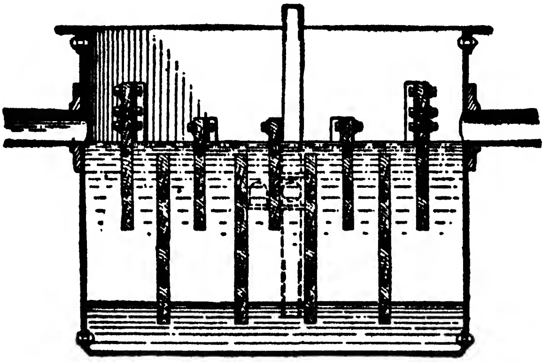

FIG. 13. Tar Separator.

Removal of Hydrogen Sulfide—The partially purified gas now contains hydrogen sulfide as its principal impurity. This is generally removed by passing it through large vessels, called purifiers, Figure 14, where it is brought into contact with some form of ferric oxide. There is considerable discussion as to the exact reactions which take place. The probable reactions are

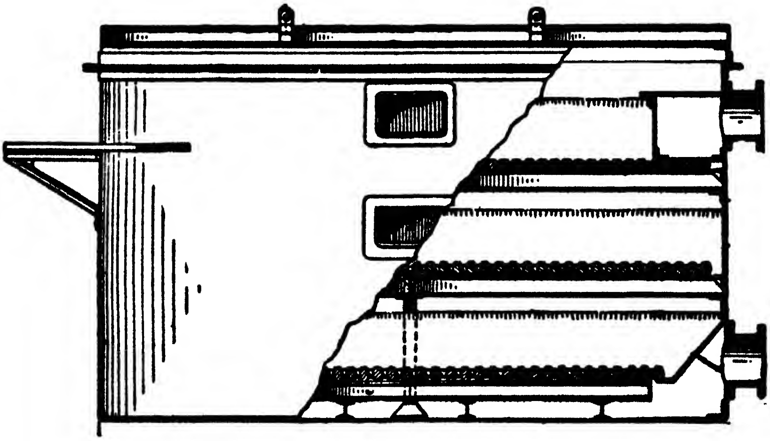

FIG. 14. Dry-seal Purifier. Deep Cheese-box Type.

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$$

and

$$Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O.$$

It seems likely that these two reactions take place simultaneously, and the proportions of ferric and ferrous sulfide formed are dependent upon the nature of the oxide and the other conditions. It is said to be in the relation of three parts ferric to five parts ferrous sulfide. When the oxide has become saturated it is removed from the purifiers and exposed to the air, where, under the influence of the atmospheric oxygen, ferric oxide is formed and free sulfur set free.

In order to take advantage of this reaction, small quantities of air are sometimes admitted to the crude gas before entering the purifiers, the oxygen in which reacts with the partially fouled purifying material, and thus considerably increases the length of time before it is necessary to remove it.

In some plants the oxide is revivified while in place by circulating through the box air or a gas mixture containing at first a very small percentage of free oxygen. The heat given off in the revivification is removed by cooling usually with a water spray so that the purifier is thoroughly saturated with water vapor; as the revivification proceeds the amount of oxygen is allowed to increase. In this manner under very careful operating control it is possible to increase the sulfur in the oxide up to 40 per cent without removing it from the purifying vessel. With certain classes of oxide it is exceedingly difficult to carry this out without danger of local superheating taking place with a resulting rise in temperature of the oxide to such a point that the oxide is destroyed.

Taking into consideration the relative costs of removing, revivifying and replacing oxide as compared to the cost of new oxide, it would appear that the most efficient operation should aim to build up the maximum content of sulfur so that when it is necessary to remove the oxide it can be discarded With the present oxides the amount of sulfur formed is so great that the oxide tends to become so compact in the purifying box that excessive back pressures set up and this limits the use of the material rather than its complete saturation with sulfur.

Essential Character of the Oxide. The purifying material is composed of either a natural ferric oxide or, as is generally the case, made by coating shavings, planer chips or corn cobs with some form of ferric oxide.

The efficiency of the purifying material thus made seems to depend upon the nature of the ferric oxide; the more active oxides are apparently colloidal in nature. Where the oxide is made by rusting iron borings on the chips the organic acids in the wood act as protective colloids and result in the formation of varying percentages of the iron in the colloidal form.

Table 16 gives analyses of a number of commercial iron oxides used for purification purposes.

Certain natural oxides and some of the artificial oxides that are by-products in the manufacture of alums are found to have a considerable proportion of their iron content in the form of a hydrogel of ferric hydroxide. Apparently it is the enormous surface that is presented by these colloidal oxides that explains the increased chemical efficiency of oxides in this state.

Study of the efficiency of different types of oxide has indicated a considerable difference in the rate at which they will absorb hydrogen sulfide and especially the completeness with which small traces will be absorbed. Where a large purifying area is available the slower-acting oxides can be used quite efficiently but where the purifying area is relatively small the more active oxides must be used for the efficient removal of the last traces of hydrogen sulfide.

Types of Oxide Boxes. In the older type of purifiers the oxide was contained in shallow cast-iron boxes provided with water-sealed lids, the oxide being carried on wooden trays in two layers of about 30 inches each. These boxes were usually arranged in sets of four or six, and so connected with valves that the sequence of boxes could be varied at will, and any box could be removed from service for cleaning.

TABLE 16—ANALYSES OF IRON OXIDES USED FOR PURIFICATION

Sample	*1*	*2*	*3*	*4*
Moisture as Received	7.0	46.0	49.5	16.5
Composition on a Dry Basis				
Fe_2O_3	78.8	75.6	48.7	48.3
Al_2O_3	0.8	1.4	5.0	0.8
TiO_2	0.4	0.8	5.0	2.0
CaO	tr	nil	8.8	12.5
MgO	nil	nil	nil	1.7
Na_2O	3.0	0.1	1.8	0.1
SiO_2	5.3	4.9	7.3	7.2
CO_2	0.8	nil	2.4	2.1
SO_3	1.5	0.1	0.3	15.7
Loss in Ignition	5.6	15.8	14.6	20.5
Alkalinity as Na_2CO_3	2.5	nil	2.9	0.9
Kunberger Test 50% Moisture	90.3	179.4	108.4	74.6
Activity Coefficient	157	5	23×9	27

It has now been found more economical to put the oxide into only two or three large boxes, building these either of steel or concrete out of doors, and thus saving expensive buildings.

Figure 14 shows a cross-section elevation of a modern type of purifying box.

Widely divergent views are held as to whether it is the time of contact, the velocity of flow, or the total volume of the oxide in use that is the determining factor in calculating the apparatus necessary for the purification of the gas. It is usually estimated, however, that with the use of a low velocity a certain total volume of purifying material is required.

In the older type of purifiers, using a number of boxes of relatively large area, with layers of oxide from 3 to 5 ft. in depth, it was usually assumed that 1 sq. ft. of area in a box would purify about 1500 cu. ft. of coal gas per 24 hours. At present, the tendency is to concentrate the oxide in two or three large circular boxes where the oxide is 10 to 15 ft. deep. Here the usual allowance is about 300 cu. ft. of gas per cubic foot of oxide per 24 hours.

In testing the operation of the purifiers, we find that the first box removes the greater portion of the hydrogen sulfide, and that as the percentage of sulfur decreases it becomes increasingly difficult to remove it. The purifiers are usually arranged, therefore, so that at least one box is kept filled with fresh and active oxide to remove slight traces of hydrogen sulfide which might pass through the other boxes which remove the bulk of the impurity.

Practical experience has indicated that, when the free sulfur formed in the oxide increases to from 40 to 50 per cent, the efficiency of the oxide was greatly reduced. It was generally assumed that the free sulfur actually coated the oxide. Microscopic examination, however, appears to indicate that the free sulfur as formed does not crystallize directly over the oxide but adjacent to it and that the small crystals first formed increase in size rather than in number.

The older and less efficient forms of oxide require from ten to twenty revivifications before they are saturated while the later colloidal oxides require from three to five.

When the cyanogen is not removed it combines with some of the iron, forming Prussian blue; this takes place at the surface, and further reduces the efficiency of the oxide.

Removal of Nitric Oxide. The harmful effects of nitric oxide in the distribution system require very careful control in the works to insure that a minimum quantity, which should never exceed 0.015 grains per hundred cubic feet, is present at the outlet of the holder.

Apparently the most satisfactory method of securing the elimination of nitric oxide in the works is in connection with the proper operation of the purifiers. Nitric oxide will react with iron sulfide, forming a more or less stable compound. For maximum removal, however, the reaction, which takes place primarily on the surface, requires a maximum percentage of iron sulfide and a minimum percentage of oxygen. The best results would be obtained if a fully sulfided box could be placed ahead of the regular purifying train and any oxygen required for proper operation of the purifying in the removal of hydrogen sulfide were admitted after this box.

Liquid Purification Systems—During recent years several systems of liquid purification have been developed. These may be divided into two general types: the systems in which the gas is scrubbed with an alkaline solution with which the hydrogen sulfide forms a very weak combination that can be broken up by the use either of air or steam; and secondly, the systems in which the hydrogen sulfide forms a chemical compound with the scrubbing solution of such a nature that when finely divided air is passed into the solution the compound is broken up, free sulfur is formed, and the original solution regenerated.

Representative of the first type is the so-called Seaboard process developed by the Koppers Company in which the gas is scrubbed with a solution containing 2 or 3 per cent of sodium carbonate or soda ash. The so-called foul solution is then sprayed into a tower known as the actifier where it meets a rising stream of air. The hydrogen sulfide absorbed is driven off as such. This system is relatively simple in installation and operation but is subject to the serious handicap of polluting the atmosphere unless some means of disposing of the air is available. In some cases this air has been used under boilers or in producers, under which conditions the hydrogen sulfide is burned, forming sulfur dioxide, which is not as poisonous or corrosive as the hydrogen sulfide.

Another example is the sodium phenolate process also developed by the Koppers Company. The gas is scrubbed with a solution of sodium phenolate and the solution is then boiled and the steam evolved drives off the hydrogen sulfide. The steam is condensed so that the sulfur is recovered as nearly pure hydrogen sulfide and can be burned for use in the production of sulfuric acid. This process is more expensive to operate than the so-called Seaboard process

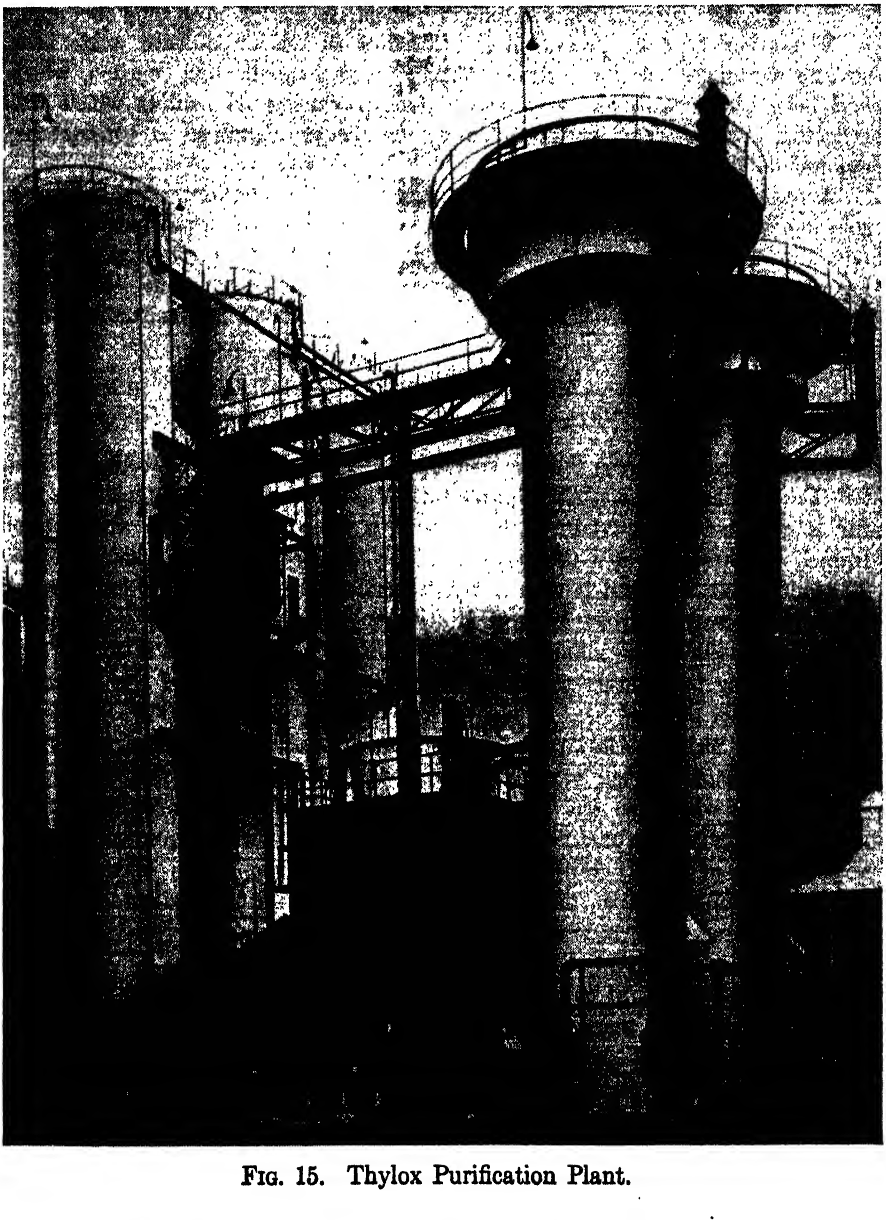

Fig. 15. Thylox Purification Plant.

but it can be used satisfactorily for gases containing high concentrations of hydrogen sulfide and the hydrogen sulfide can be utilized.

Another process of this type is known as the "Girbotol," in which the gas is scrubbed with a solution of triethanolamine, which is an organic base that readily absorbs any acidic gas such as hydrogen sulfide, which is, in turn, released upon heating. This process also permits the recovery of hydrogen sulfide in relatively pure form. However, it has the disadvantage that the organic base is relatively expensive.

Still another process utilizes sodium phosphate as the absorbing medium.

The other type of process first utilized a suspension of iron oxide in a sodium carbonate solution. Under suitable conditions the foul solution, which had been blown with air, was regenerated, producing free sulfur which was collected and removed as a sludge which always contained a considerable amount of the iron oxide.

A recent modification of the process known as the Thylox process utilizes a solution of sodium arsenite. When this compound reacts with hydrogen sulfide it forms sodium thioarsenite, which is converted by air into sodium thioarsenate. The thioarsenate solution absorbs the hydrogen sulfide, then when subjected to oxygen, is regenerated with the formation of free sulfur as shown by the equations:

$$Na_4As_2S_5O_2 + H_2S = Na_4As_2S_6O + H_2O \qquad \text{(absorption)}$$

$$Na_4As_2S_6O + O = Na_4As_2S_5O_2 + S \qquad \text{(regeneration)}$$

In the Thylox process the reaction is carried out at a temperature of about 95° F. The solution contains approximately .75 per cent of As_2O_3. The sulfur is collected by flotation at the top of a tall tower and the slurry thus formed is dewatered in a filter press, usually of the continuous vacuum type. The sulfur thus obtained is very finely divided and has found a certain amount of use as a dusting agent for agricultural purposes or it may be melted into bricks and used in the manufacture of sulfuric acid. It has been found possible by using two towers to secure nearly complete removal of the hydrogen sulfide by this process.

Organic Sulfur—Only part of the sulfur is in the gas as hydrogen sulfide. Very appreciable though varying proportions occur as organic sulfides.

Formerly when the gas was purified with slaked lime, partially sulfided lime reacted with the organic sulfur compounds, and thus removed a considerable portion of them. With the present almost universal use of iron oxide, however, a much smaller proportion of the organic sulfur is taken out. The small percentage that is removed is undoubtedly due to its solvent action on the free sulfur present in the purifying materials.

The extensive use of gas in many industrial operations where it may come in contact with the material to be treated has caused more interest in the removal of the small quantities of organic sulfur which are not removed in the ordinary oxide purification. The organic sulfur compounds present in the gas consist in large part of carbon disulfide but there also exists 3 to 7 grains per hundred cubic feet of other organic sulfur compounds that are quite refractory and difficult to remove. The most successful processes have been those involving treating the gas at an elevated temperature with some catalyst.

One of the earliest processes used in England employed nickel as a catalyst with the gas at a temperature of 750° F. This process only removed the carbon disulfide, which combined with the hydrogen present in the gas, forming two molecules of hydrogen sulfide and setting carbon free, which deposited on the catalyst and had to be burned off periodically.

Another process, originated in the United States, uses colloidal ferric hydroxide at a temperature of about 450° F., the gas containing a certain amount of water vapor. In this process the carbon disulfide forms hydrogen sulfide and carbon dioxide, which are subsequently removed. Another process uses a special catalyst and operates at a temperature of about 500° F. This process also forms hydrogen sulfide but reduces the organic sulfur to below 2 grains per hundred cubic feet. The catalyst is so active that small quantities of unsaturated hydrocarbons present are apparently decomposed, depositing carbon which must be removed by burning off with air at intervals of from 5 to 7 days.

Benzol Enrichment—Where coke oven gas is supplied for distribution, the heating value is subject to fluctuation and where it is used without admixture with carbureted water gas it is necessary to have some means of maintaining the heating value of the gas at the desired standard.

Where the light oil (a mixture of benzol, toluol, and xylenes) is not removed, the heating value is usually above the standard required, and this is reduced by the admixture of producer gas. On the other hand, where light oil recovery plants are in operation the heating value of the scrubbed gas may be low and will require enrichment. For controlling the value, therefore, the admixture of benzol vapor is convenient and satisfactory.

Theoretically, coal gas should be able to carry about 3.5 per cent by volume of benzol vapor at 32° F.; as coal gas usually contains from 0.5 to 1.0 per cent, it would carry an addition of, say, 2.5 to 3 per cent of vapor and this would correspond to an increase in heating value of 93 to 150 B.T.U. Practically, however, it is difficult to secure an increase of much over 75 B.T.U. This is due to the varying composition and vapor tension of the components of the commercial benzol used and to the vapors already present in the gas.

The heating value of the benzol used for enrichment averages about 17,000 B.T.U. per pound and it will weigh 7.3 lbs. per gallon, giving from 124,000 to 125,000 B.T.U. per gallon, or one gallon per thousand should give 125 B.T.U. per cubic foot increase. It is frequently difficult to carry over 100 to 110 B.T.U. per cubic foot, as some of the hydrocarbons are deposited in the mains and drips.

The benzol used for enriching purposes is usually a "crude 90 per cent" benzol and will have the following distillation characteristics:

First drop	76 to 78° C.
80° C.	2 to 5%
90° C.	50 to 70%
100° C.	85 to 90%
Dry	145 to 165° C.

The amount distilling up to 80° should be as low as possible as it will generally be high in sulfur and a high dry point is disadvantageous because it will give trouble in the vaporizer and lower the efficiency.

The benzol is vaporized by passing it over steam coils in a cast-iron vessel. In some cases live steam is added to assist in carrying the vapors into the main where it is mixed with the gas, but better results are generally obtained by passing a small fraction of the gas at higher pressure through the vaporizer and using this to carry the vapors into the steam main. The vaporizer should be located as close to the main as possible.

CARBURETED WATER GAS

Though coal gas was historically the first manufactured gas for many years, carbureted water gas, due to its lower investment cost and more flexible operation, has perhaps been the most important. The relative economic advantages of coal gas and carbureted water gas are largely dependent upon the existing local conditions and many factors must be given consideration. In the past, the high value of the residuals obtained in the manufacture of coal gas outweighed the greater investment and operating cost of the coal gas process. At present, however, in many situations carbureted water gas has become the more economical gas, particularly for smaller plants because of the extension of the use of by-product coke ovens, and the large volumes of coke which had to be disposed of resulted in very keen competition for the coke market. Other economic features were the practical elimination of ammonia, as a credit due to the development of synthetic ammonia plants, and the general increase in the cost of operating labor.

In the desire to secure the lowest and most efficient operation, many modifications of the older process have been developed, such as the use of cheaper fuel oil for enriching purposes, the very general use of bituminous coal rather than more expensive coals, and the adoption of automatic self-clinkering generator grates which have contributed to more uniform operation and lower operating labor costs.

Reactions in the Formation of Water Gas—The manufacture of water gas depends upon the decomposition of steam in contact with incandescent carbon. This reaction has been known for many years but its practical application did not take place until the latter part of the nineteenth century. When steam is decomposed by carbon, approximately equal quantities of carbon monoxide and hydrogen should be produced. Such a gas is called "blue gas," and while it has a high flame temperature its heating value is usually between 290 and 300 B.T.U. per M.C.F. so that it is necessary to enrich it by the addition of some gaseous hydrocarbon or vapors in order to bring it up to the standard required for distribution. This process of carbureting or enriching is given the name of "carbureted water gas."

The reaction between steam and carbon is strongly endothermic. The heat required is obtained and stored in the fuel bed itself by combustion of a portion of the fuel with air. The process therefore becomes a cyclical one and is divided into the two steps: (1) the blow during which heat is stored up in the fuel bed and in the vessels used for carburetion with the enriching oil, and (2) the run or the heat-absorbing portion of the cycle where the steam is decomposed and the blue gas formed and enriched.

Theory of the Formation of Blue Gas—In considering the theory of the formation of the blue gas or water gas proper we have the two general steps: storing heat in the fuel bed by the combustion of a portion of the fuel with a blast of air, and utilizing this heat in decomposing steam with the formation of the water gas, which is an endothermic reaction.

Reactions with Air. There is still some disagreement as to the actual mechanism of the combustion of carbon with air. This has to do primarily with the question as to whether carbon monoxide or carbon dioxide is the primary product. It may very well be that there is a formation of both carbon monoxide and carbon dioxide, but the carbon monoxide is immediately oxidized to carbon dioxide in the presence of free oxygen and experiments have indicated that there is no appreciable carbon monoxide present until all of the oxygen has been consumed. This takes place in a rather narrow zone where the maximum temperature is reached. From this point on there is a reduction of the carbon dioxide to carbon monoxide.

During the blasting period the primary reaction is probably:

$$C + O_2 = CO_2 \quad \text{or} \quad 2C + O_2 = 2CO.$$

These equations are connected by relation $CO_2 + C = 2CO$, which is the equation for the equilibrium. Clement and Haskins have given the following expression for the value of K at any temperature, viz.:

$$K = \frac{C_{(CO^2)}}{C_{(CO_2)}}.$$

$$\ln K = -\frac{20235}{T} + 1.035 \ln T - .001564T + 8.604.$$

The equilibrium percentages with coke at different temperatures:

TABLE 17—EQUILIBRIUM BETWEEN COKE, CO AND CO_2

Temperature	*Carbon Monoxide*	*Carbon Dioxide*
° *C.*	%	%
900	83.2	16.8
1000	94.5	5.5
1100	98.1	1.9
1200	99.4	.6
1300	99.7	.3

It must be remembered, however, that in commercial producer gas the presence of the nitrogen lowers the partial pressure of the carbon monoxide, and thus slightly increases the ratio $CO \div CO_2$ over that given in the table. It is found that the time of contact is very important, and that with the increasing temperatures the increase in the coefficient of the reaction velocity is about ten times the increase in the diffusion constants, so that velocity of the chemical combination is the determining factor in this reaction.

It is found that the different forms of carbon do not react alike, charcoal reacting most rapidly, coke next, and anthracite most slowly.

Reactions with Steam. In the second stage of the process, that of the decomposition of steam, we have two reactions: $C + H_2O = CO + H_2$ and $C + 2H_2O = CO_2 + 2H_2$. These products are then related according to the two reactions $CO_2 + H_2 = CO + H_2O$, and by the reaction previously discussed, $CO_2 + C = 2CO$.

The water gas reaction at temperatures as low as 500° C. in the absence of catalyst is quite sluggish. However, the velocity increases very rapidly with the rise of temperature until at 1000° C. decomposition of steam is practically complete. The proportions of the four gases involved in the equations at equilibrium bear the following relation to each other:

$$K = \frac{CO \times H_2O}{CO_2 \times H_2}$$

An approximate value of K, corresponding to the various temperatures, can be obtained from data of the heat of reactions and the specific heats of all of the gases involved. The more recent work on this subject by Partington and Shilling has given the values in Table 18.

TABLE 18—EQUILIBRIUM CONSTANT OF THE WATER GAS REACTION

Partington and Shilling Values

Temperature ° C.	*Value of K*
600	0.33
700	0.55
800	0.85
900	1.21
1000	1.60
1100	2.02
1200	2.47
1300	2.92

The constant K is independent of the pressure but it increases rapidly with the temperature. In practice, the manufacture of water gas is carried out at about 1000° C., at which temperature the decomposition of the water vapors is practically complete and the carbon dioxide content does not exceed 2 per cent. The practical results indicate the high probability that the ash in the fuel bed acts as a catalyst, causing the reaction to adjust itself down to very moderate temperatures.

It is assumed that in the generator, while the gases may be in equilibrium with themselves, they are not in equilibrium with the carbon in the fuel bed. In Figure 16 are given some experimental results obtained by Clement and Haskins, using coke as fuel, with the time of contact of the steam equal to two seconds.

In the practical operation of water gas apparatus the efficiency of the production of blue gas will be dependent upon the temperature of the blast gas and water gas issuing from the fire; the percentage of CO or excess air in this blast gas, and the percentage of undecomposed steam in the blue gas, assuming, of course, that we are operating the generator so as to produce a reasonably low percentage of CO_2. These conditions will probably be influenced by the rate and time of passage of blast through the fire. There are two divergent views on this subject. According to one writer, when the rate of passage of blast is sufficiently great in proportion to the depth of fuel, CO will not be formed, but only CO_2. Another writer, on the other hand, finds very little change due to the rate of passage of the gas, and believes that the efficiency of the blow is dependent on the temperature of the fire and is principally a function of the length of time.

Apparently, an increase in the rate of blast, Figure 16, will give a higher average temperature of the fire, which results in somewhat increased temperature of the issuing blast gases, with slight decrease in the percentage of CO. It is quite conceivable in view of the theory that the speed of the reaction $CO_2 + C = 2CO$ will increase so rapidly with increase in temperature that we cannot sufficiently decrease the time of contact to prevent the formation of considerable quantities of CO.

Increasing the rate of passage of steam will apparently reduce the temperature of the outgoing water gas, which is favorable to economy, but this is more than offset by the smaller percentages of steam decomposed, and the consequent waste of both excess steam and its sensible heat, and furthermore, by the greater percentage of CO_2 in the blue gas. In general, all of the writers assume the importance of the slow rate of passage of the steam.

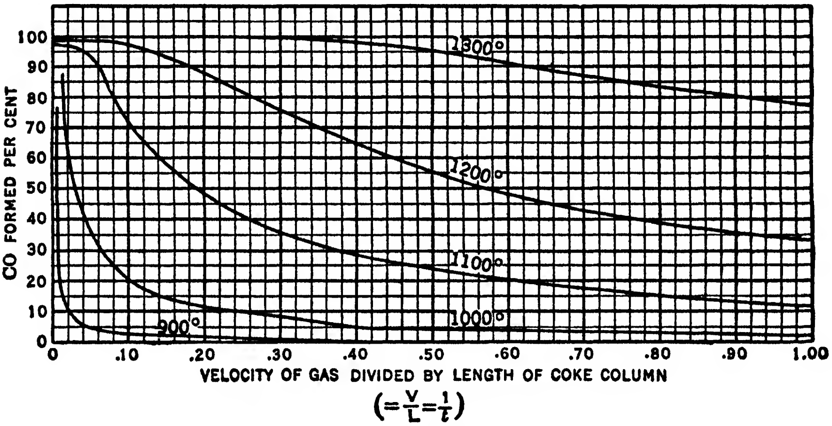

FIG. 16. Rate of Formation of Carbon Monoxide in a Producer.

Reactions During the Run—While from the theoretical standpoint the lower rate of passage of steam will result in higher percentages of decomposition, this can be secured only at the expense of a considerable reduction in the rate of production of gas per unit area and, therefore, there will be a distinct loss in capacity.

The temperature and condition of the generator fire, Figures 17 and 18, appear to be the most important conditions. The capacity of the fuel bed increases with an increase in the temperature, resulting in a larger yield and a more perfect decomposition of the steam, and a more favorable composition of the blue gas. On the other hand it increases the sensible heat of the offgoing blast products and the blue gas, and results in an increased percentage of CO in the blast products, both of which are unfavorable to fuel economy.

The necessity of producing a certain amount of available combustible in the blast gases to maintain the fixing chambers at the proper temperature somewhat complicates the operation when carbureted water gas is manufactured. With indifferent control of the operating conditions and with some fuels a large excess of CO is always produced.

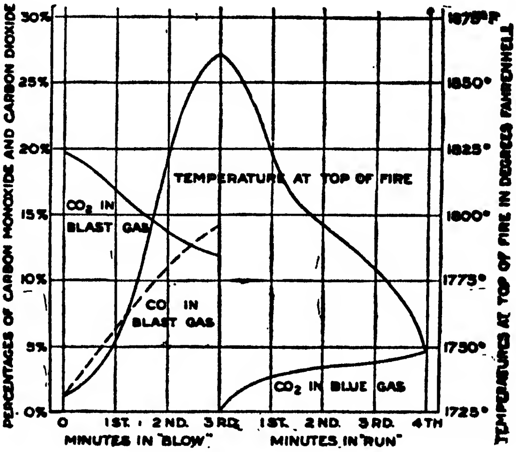

FIG. 17. Variation of Fuel Bed Conditions During Blow and Run.

Modern practice attempts to bring the whole fuel bed to a uniform temperature and to reduce the variation or range of temperatures as far as possible, thus enabling the temperature in the active zone in the fuel bed to be maintained at a point where the clinker can be controlled. This results in a

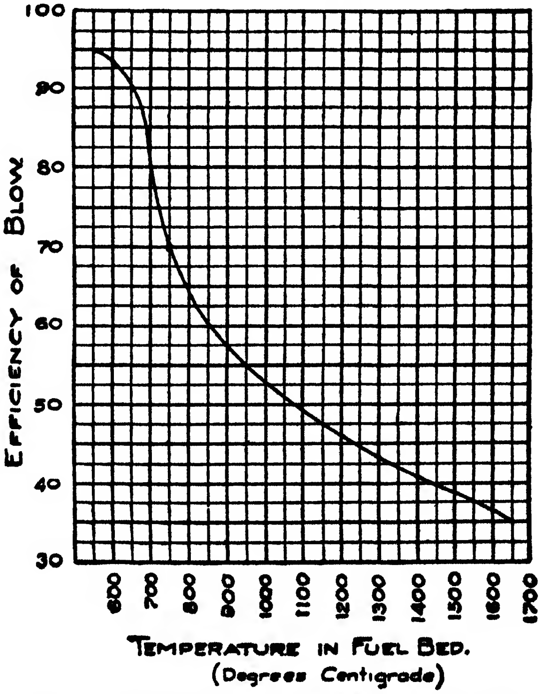

FIG. 18. Efficiency of Blow *vs.* Temperature.

minimum loss of sensible heat incurred by the offgoing gases and yet a satisfactory decomposition of the steam is secured at an increased rate.

The use of two generators that are blasted in parallel but are connected in series, during the gas-making period, was an endeavor to secure more uniform fire conditions.

From the theory of the reactions underlying the combustion of the coal and the formation of water gas, it will be seen that many of the requirements are contradictory. It is therefore necessary to arrange operating conditions to secure the most efficient compromise, remembering that many of the theoretical processes will yield very efficient results under test conditions, but may utterly fail to satisfy the commercial requirements as to overhead charges for capital invested and the labor cost of operating.

Apparatus—The modern water gas apparatus is the development of the Lowe apparatus that was patented in 1872-1875. In its present form it is very efficient, as every feature has been considered both from a theoretical and operative standpoint. The supply of air and steam is metered. The temperatures in the fixing chambers are controlled automatically by electric pyrometers and the sensible heat in the offgoing blast and illuminating gases is recovered in greater part in economizer boilers that return sufficient steam to operate the plant, and the air, steam, and oil valves that control the operation of the apparatus are all automatically manipulated in predetermined cycles.

Many modifications in water gas apparatus have been developed during the past decade. However, we shall describe here only the more generally used apparatus and method of operation.

Figure 19 shows a modern set of the cone top type. In this apparatus the generator is 11 ft. in diameter by 17 ft. 4 in. high. The carburetor is 9 ft. in diameter by 17 ft. 4 in., superheater is 10 ft. by 28 ft. 6 in. The wash box is 10 ft. in diameter by 5 ft. 4 in. Automatic operation and temperature control are provided. Such a set will have a capacity of 3,500,000 cu. ft. per day with good fuel.

Operation—The operation of water gas apparatus is as follows: The generator is charged with fuel through the coaling door at the top. After ignition it is raised to incandescence by an air blast beneath the grate. The air is supplied at a pressure of from 30 to 40 in. of water and is metered by a Venturi meter.

In passing through the fuel bed we have the reaction $C + O_2 = CO_2$ and $CO_2 + C = 2CO$. The temperature of the fuel bed rises rapidly and producer gas is formed. The products pass out of the top of the generator through a hot valve into the carburetor.

The carburetor is a fire-brick-lined vessel filled with checker brick and provided with an oil spray at the top for admitting oil.

In the connection between the generator and carbureter is a blast connection so that the producer gas from the generator can be burned in the carburetor, thus raising its temperature to that required for the process. From the bottom of the carburetor the products pass up through the superheater and out through the stack valve to the stack. The superheater is filled with checker brick and is somewhat higher than the carburetor. Air may be admitted at the base of the superheater if required. At the top of the superheater is a large connection to the wash box.

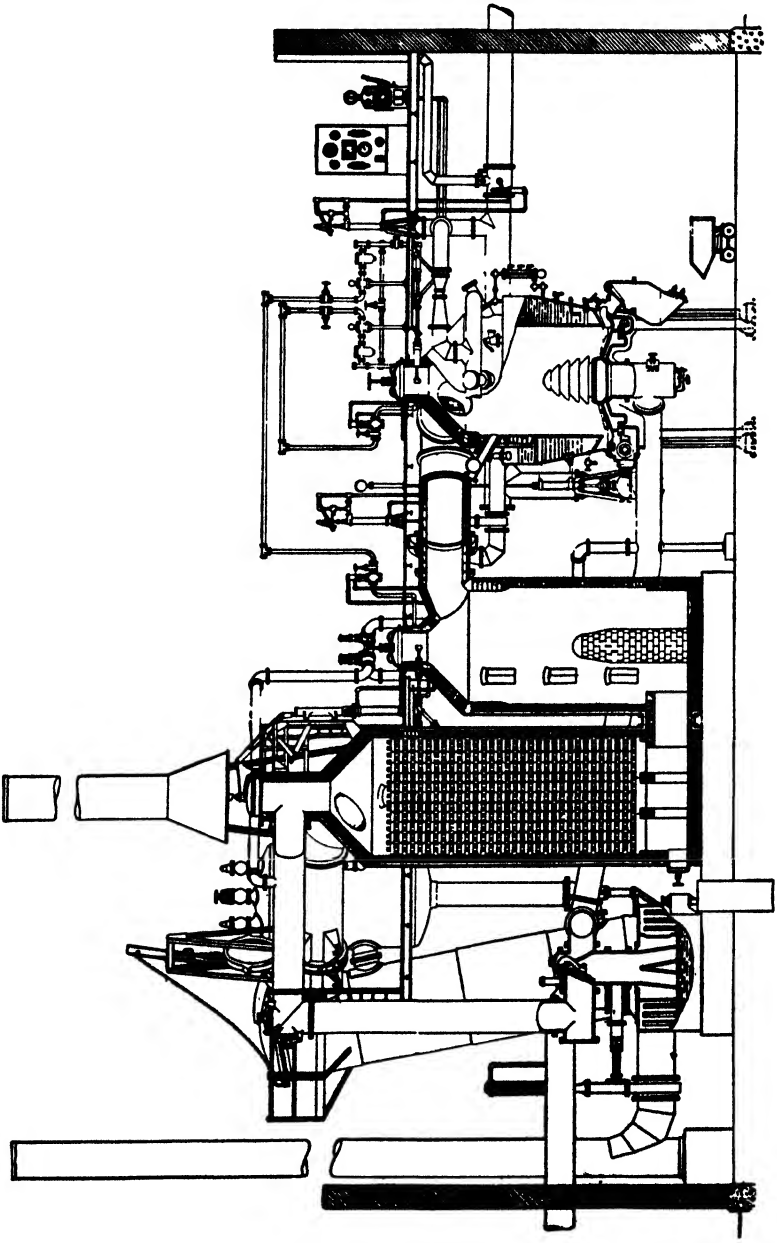

FIG. 19. U. G. I. Mechanical Generator Carbureted Water Gas Apparatus.

Automatic Grates—Two rather different designs have been developed for the automatic removal of clinker. There is a common type of generator in which the grate is in the form of a tuyère and the whole bottom of the generator revolves slowly. The stationary portion of the generator is water-

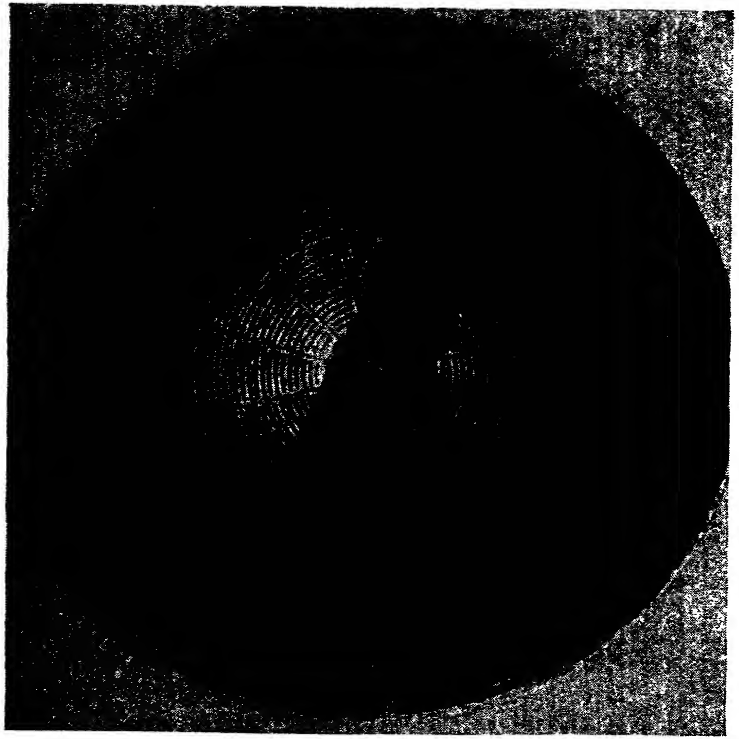

FIG. 20. View of Beam in A. B. C. Grate Looking Down from Charging Door.

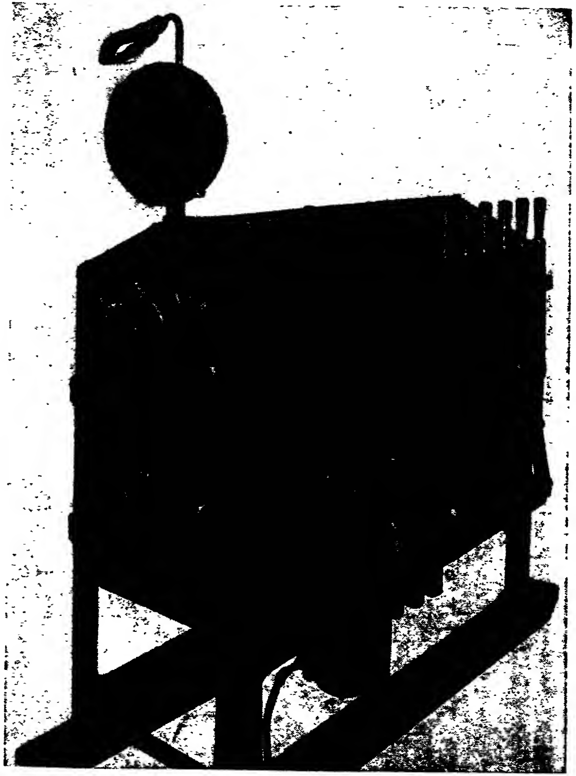

FIG. 21. Automatic Control for the Operation of Carburetted Water Gas or Blue Water Gas Apparatus.

jacketed from a boiler which produces a considerable proportion of the steam needed in the operation and, being water-cooled, no clinker will adhere to the walls.

Figure 20 shows another type in which the grate proper is stationary, but an arm is intermittently moved across the top of the grate, cutting off and crushing any clinker which may be formed. In this design, the walls are not water-cooled but are lined with refractory material which is cooled by radiation.

The use of the automatic grate has resulted in considerable saving in operating labor and in the production of more uniform fire conditions and increased operating time due to the elimination of the time formerly required for the removal of the clinker.

An important modification in the usual apparatus has been the introduction of the so-called "back run" process. This consists in the use of valve connections from the bottom of the generator directly to the wash box. The reverse connection between the top and bottom of the generator and the top hot valve are removed and a valve is put in between the top of the superheater and the wash box.

In operation, during the blow the valve on the back run connection to wash box is closed.

The Gas Run—When the carburetor and superheater have been brought to the desired temperature, the air blast, the superheater, carburetor, and generator are cut off in the order named. The stack valve is closed and the steam is admitted through a meter beneath the grate of the generator. When the steam passes up through the hot fuel it is partially decomposed, forming blue water gas in accordance with the reaction $C + H_2O = CO + H_2$ and the general water gas reaction $CO + H_2O = CO_2 + H_2$.

The hot water gas passes into the carburetor where it meets the enriching oil, which is passed through a meter under pressure and then through a spray in the top of the carburetor. The sensible heat of the water gas and the high temperature in the surface of the checker bricks vaporize the oil. The mixture of water gas and oil vapors then passes down through the carburetor, where the vaporization is completed, a considerable portion of the vapors being decomposed and to some extent polymerized into fixed gases. Passing from the base of the carburetor up through the superheater, where the temperature of the checker brick is very carefully regulated, the decomposition of the oil vapors is carried to the most advantageous point. The resulting mixture is composed of fixed gases, some condensible vapors and a small quantity of complex hydrocarbons, known as water gas tar.

These pass out through the connection to the stack valve, through the dip pipe into the wash box, which acts as a hydraulic seal and prevents both the escape of the products of combustion during the blasting period and the return of the illuminating gases. In contact with the water in the wash box, the temperature of the gas is reduced from 1200° or 1300° F. to about 190° by the vaporization of the water, and some of the tar is deposited. The gases pass out of the wash box through the scrubbing and condensing apparatus to the relief holder.

The Cycles. The operation is a cyclical one. The first portion or heating-up period is known as the "blow" and the latter portion or "making period" is known as the "run."

At the end of the run the oil is shut off and, after the set is cleared of oil vapors and steam, the stack valve is opened and the "blow" is commenced.

The relative length of the run and blow is determined by the quality of gas to be made and the fuel used. There is a tendency to reduce the length of the cycle as far as possible and with automatic operation the "blow" may be from 1 to 1.5 minutes and the run from 2.5 to 3.5 minutes.

In order better to control the condition of the fire, the generator is equipped with valved connections so that during the run the steam may be put into at the top, and pass down through, the generator then up through the connection to the carburetor. This is known as a "down" run.

The relative proportion of "up" and "down" runs is determined by the character of the fuel, principally its tendency to clinker.

The generator is usually charged with fuel every hour and depending upon the ash in the fuel the apparatus is shut down and the clinker removed from the generator once to three times a day. The removal of the clinker is arduous work and many experiments have been made with mechanical grates designed to remove the clinker continuously.

Introduction of Oil—All of the oil is introduced during the first portion of the run that is made "up." The oil and bottom steam are then shut off; the back run valve is opened and the valve between the superheater and wash box is closed. Steam is then introduced at the top of the superheater and passes down and up through the carburetor, becoming superheated, then down through the generator making the "down" portion of the run. The blue gas thus made passes through the back run connection to the wash box.

By operating in this manner a saving of 3 to 4 pounds of generator fuel is secured, but about 0.1 gallon more oil is required. Apparently this saving is partially due to the heat that would be taken from the carbureting vessels by the cold blue gas on the "down" run and to the action of the superheated steam.

In the "Generator Down Run" system the top hot valve and bottom hot valve are retained but the connection between them is removed and the bottom hot valve is connected to the wash box. During the blow the top hot valve is open and the bottom hot valve is closed. The oil is introduced as in the "back run" process during the first of the "up" portion of the run. During the "down" portion of the run the top hot valve is closed and the bottom valve opened, the steam being introduced at the top of the generator above the fire.

A slightly smaller saving of generator fuel is obtained with this system than with the "back run" but the oil results are better due to the fact that the carburetor and superheater are not cooled by the "down" steam. This also results in a saving in the air required during the blow. The relative economies of the two systems will naturally depend upon the prices for generator fuel and oil.

Use of Bituminous Coal—An important change in operating methods was the use of bituminous coal instead of coke in the generators. The impelling reason was the high cost of coke in the middle western states and the low cost of bituminous coal. When bituminous coal is used alone the capacity of the apparatus is considerably reduced, but by using some coke, depending upon the character of the coal, practically the standard capacity of the set can be obtained, together with an actual reduction in the total generator fuel.

When good grades of gas coal are used very successful results are now being obtained with 80 per cent coal, 20 per cent coke, maintaining the same capacity as with coke and securing satisfactory oil results.

An important factor in the use of bituminous coal is the action of the coal in the hot zone at the top of the generator. Apparently the best results are obtained with coals of the splint type, that is, those that are not too strongly coking. The sizing of the coal is also important and the complete removal of all small coal and slag is essential in order to maintain satisfactory fire conditions. Apparently, the best results are obtained with lump coal known as "3 x 8," that is, passing through 8-in. bars and retained on 3-in. bars. It is very important of course that the coal should not decrepitate when suddenly heated.

Apparently in operating with bituminous coal the active portion of the fuel bed is an annular ring around the circumference so that the smaller-size generators give better results than the larger ones. This observation has been utilized in what is known as the "Pier" process of utilizing bituminous coal. In this system a solid cylindrical pier of refractory material is built on the grate of the generator of such a diameter that the annular ring of fuel thus formed varies from 26 in. in width in the smaller generators to 36 in. in the larger sizes. This permits the use of all bituminous coal with about 90 per cent of capacity of the generator with coke.

An important feature in connection with the use of bituminous coal is the use of the so-called "blow-run." About fifteen seconds before the close of the blow the carburetor air is shut off and the stack valve is closed, thus sending the rich producer gas into the make gas.

Due to the coal gas produced during the blow, the producer gas is much richer when coal is used in place of coke. It may range in heating values up to 150 to 160 B.T.U. per cubic foot. This increased heating value would result in overheating the carburetor and superheater if all of it were consumed by the secondary air, so the use of a certain amount of blow-run is almost essential to prevent overheating or the emission of smoke if insufficient secondary air is used.

The data of Table 19 give the operating conditions at two plants, one operating on coke alone and the other on approximately 80 per cent bituminous coal and 20 per cent coke. This will give an idea of the variations necessary with the two fuels.

Automatic Control—The use of the automatic control of the set operation has contributed largely to the increasing efficiency of water-gas operation as it permits the use of very short and precise cycles that cannot be obtained by manual operation. Figure 21 shows one of the standard models of the automatic control.

In this apparatus two shafts are evolved, by means of an electric motor, through a cone gear at any desired rate to give the cycle of operation—

i.e., 3-4-5-6-7 minutes. One shaft controls the operation of the blow and the other controls the operation of the run. These two are geared so that their zero point, which always coincides, is the point at which the stock valve is opened or closed. All the other operations can be adjusted by means of clutches shown as two dials in the print of the apparatus, so that they may take place at any desired point in the cycle.

By means of these adjustable cams, pawls are operated which engage rocking arms that open or close the desired hydraulic valves that control the actual apparatus. By cutting off the electric current, the machine automatically comes into the "off" position, so distant control is readily provided.

TABLE 19—OPERATING DATA OF COAL AND COKE PRODUCER PLANTS

	100% Coke	*80% Boiler Coal, 20% Coke*
Heating value gas	540 B.T.U.	542 B.T.U.
Oil, per M	2.91 gallons	3.10 gallons
B.T.U. per gallon	99.6	95.0
Fuel, per M	30.6 lbs.	30.1 lbs.
Fixing temperature	1410° F.	1450° F.
Blow	2.35 minutes	3.0 minutes
Run	3.00 minutes	3.0 minutes
Per cent down runs	34%	28%
Generator air, per M	1520 cu. ft.	1350 cu. ft.
Steam, per M	33 lbs.	28 lbs.
Gas made per sq. ft. grate per hr.	2150 cu. ft.	1975 cu. ft.

The temperature in the fixing vessels is automatically controlled by cutting off the blast if the temperature is too high or continuing it until the proper point is reached. The automatic control not only does everything that a man could do, but does it faster and has the advantage of not forgetting.

Waste Heat Boilers—An important economy in operation can be secured by the use of waste heat boilers that will recover the greater portion of the sensible heat in the new blast products. A vertical type is ordinarily used. This is located at the outlet of the superheater and will recover approximately 25 to 30 pounds of steam per M.C.F. of gas produced.

While boilers have been used that recover the sensible heat in the make gas, they are subject to a considerable amount of carbon deposit which tends to coat the tubes, reducing their efficiency and requiring very frequent cleaning so, in general, only the blast gas boilers are now used.

Use of Heavier Oil—An important modification of the apparatus has been developed to permit the use of the heavy carbon-bearing fuel oils for enriching purposes. Due to the demand for gasoline, the usual gas oil has been used for cracking, which has restricted the supply so that the gas industry has been forced to adapt itself to the use of cheaper grades of oil, such as fuel oil. These oils carry a considerable amount of material that will deposit carbon in quantities up to as high as 15 per cent and their use on checker brick would rapidly clog up the interstices. One method of handling these high coke-bearing oils has been to atomize the oil at high temperature and under considerable pressure into an empty carburetor. The oil is vaporized by the heat from the walls of the carburetor and the coke is deposited in the bottom where it can be removed through appropriate doors. A small pier of checker brick is built in the bottom to provide an igniting source for the producer gases. Other modifications use an arch for ignition.

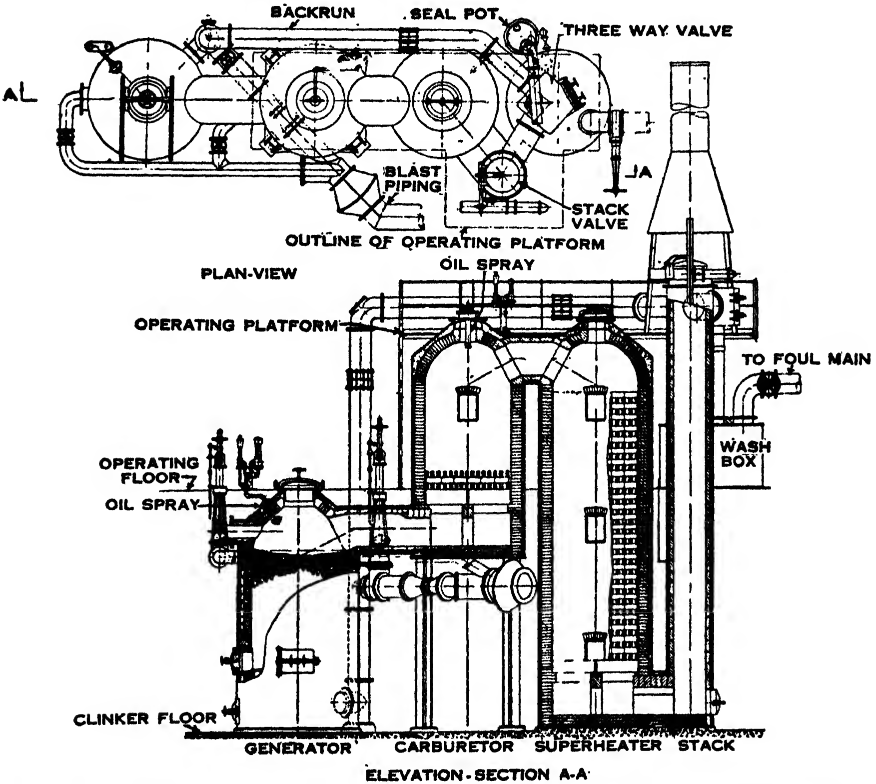

Fig. 22. Apparatus for Reversed Flow Process for Carbureted Water Gas.

In addition to being fed into the carburetor, a portion of the oil is sprayed on the generator fire and the coke that is deposited is utilized as generator fuel. This type of operation requires that the top of the fire shall be at a relatively high temperature to insure complete vaporization of the oil, both to promote efficiency and to prevent smoke. The air required for the secondary combustion is introduced in a series of nozzles around the generator just above the level of the fuel. This system is known as marginal blast.

Reforming. Under certain conditions the relative prices of fuel oil and coke are such that it is economical to increase the amount of oil used on the fire with a resulting decrease in the required amount of coke for generator fuel. This is done by injecting a certain portion of the oil on the down run with the result that it passes through the hot fuel bed and is almost completely decomposed into its elements; carbon is deposited and burned as fuel and the hydrogen which passes through causes a considerable decrease in the specific gravity of the final gas. This process is known as "reforming" and by its use a great deal of flexibility is secured in controlling the relative amounts of enriching oil in the generator fuel and in the production of gas of almost any desired heating value and specific gravity.

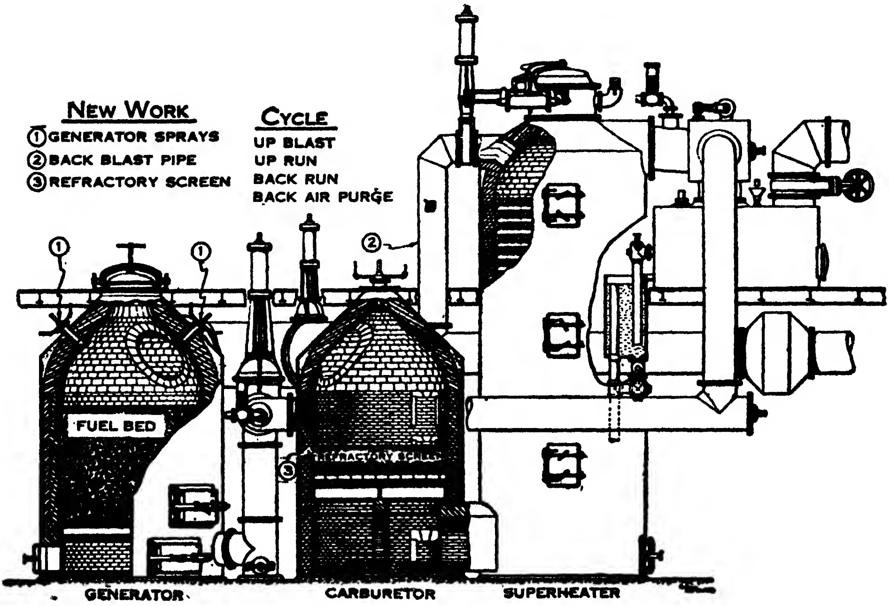

Fig. 23. Refractory Screen Carburetor.

Reversed Flow Operation. Another modification is known as the "reversed flow" operation, which is shown in Figure 22. In this scheme the direction of the flow of gas in the carburetor, which is normally from the top down, is reversed by elevating the carburetor so that the blast gases enter at the bottom. This permits the oil to flow downwards against the rising stream of hot blue gas.

The third modification uses a bed of refractory material in the ordinary carburetor to retain the coke formed where heavy oil is used. This is shown in Figure 23.

Figure 24 gives the plan of a moderate-sized water gas plant. It will be noted that the gas passes from the generator through the preliminary scrubbers and condensers to the relief holder, hence through the final condensers, exhauster, through the purifiers, meter, and storage holder, then through the governor to the distribution system.

Detailed Consideration of Solid Fuels Used—The fuels used in the manufacture of water gas are anthracite and bituminous coal and the various grades of coke. Owing to its cost, the use of anthracite is rapidly decreasing, and the use of bituminous coal is rapidly increasing, and promises to supplant a considerable proportion of the coke.

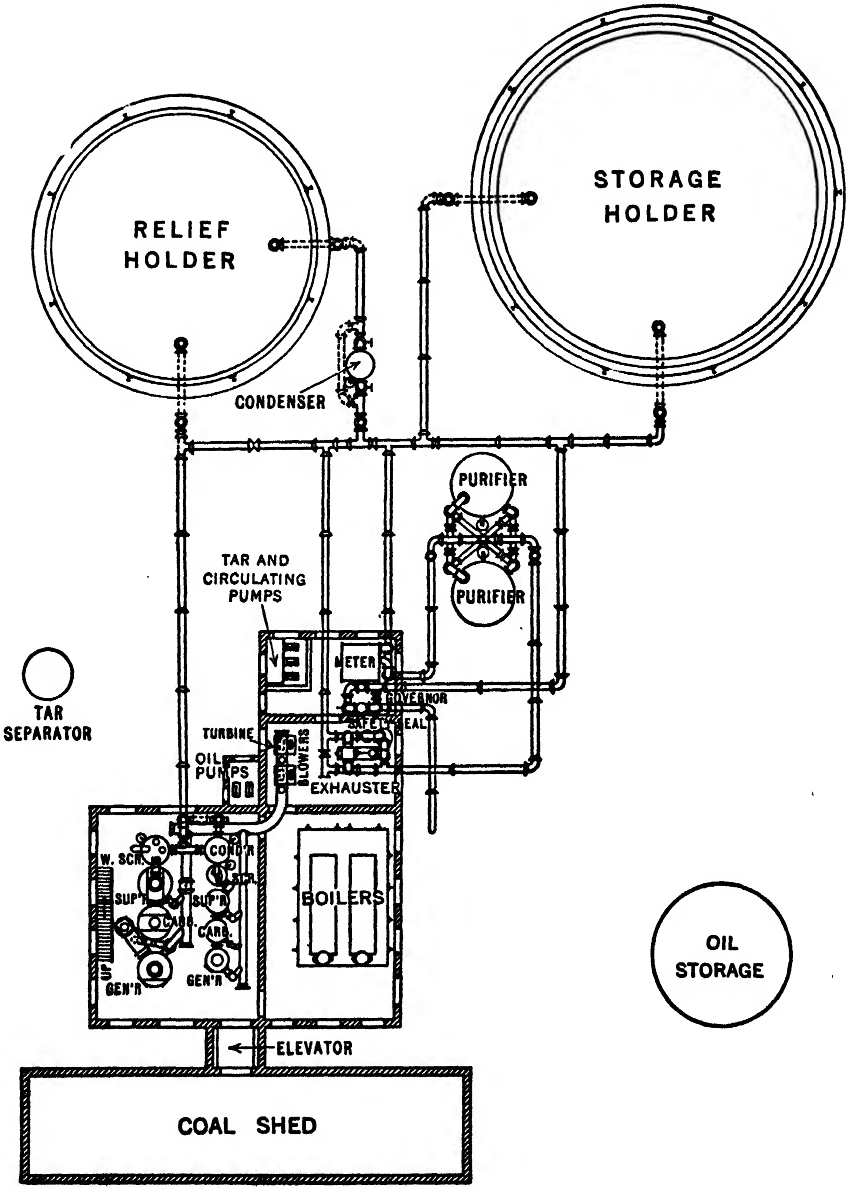

Fig. 24. Plan—Water Gas Plant.

From a theoretical viewpoint the important function of the fuel in a water gas generator is to generate and store up the maximum amount of heat in a very short interval of time. Consequently, the denser cokes would theoretically be better because they have the higher heat-storing capacity.

On the other hand the texture of the coke should be such that it will react readily with the air and steam so the maximum velocity can be attained.

The principal requirement of all fuels is that the ash should be low, so excessive amounts of clinker will not be formed and that the fusing point should not be too low, so that the clinker can be controlled or that it not be too high, as such fuels cause clinkers to form in the upper part of the fuel bed that are difficult to remove and must be cut off with bars from the coaling door. Ash with a fusion point from 2300° to 2450° F. appears to give the most satisfactory operation.

Table 20 gives an analysis of typical commercial generator fuels.

TABLE 20—COMMERCIAL GENERATOR FUELS

	Moisture %	*Volatile Comb.* %	*Fixed Carbon* %	*Ash* %	*Sulfur* %	*Fusing Point of Ash* ° *F.*
Anthracites:						
Buck mountain	3.87	4.08	77.52	14.53	.40	2750
Lackawanna	3.92	3.48	82.11	10.49	.63	2714
Lehigh	3.44	3.11	84.11	9.34	.50	2610
Pittston	3.91	5.16	73.07	17.86	.90	2962
Susquehanna	2.30	5.00	84.14	8.56	.66	3115
Cokes:						
West Virginia	.69	.83	91.11	7.31	.49	2282
West Virginia	.80	.88	85.53	12.79	.66	2610
Virginia	.70	.86	90.81	7.63	.46	2606
Alabama	.60	.69	87.01	11.70	.77	2715
Kentucky	.02	.56	94.58	4.84	1.04	2250
Bituminous coals:						
West Virginia	2.5	35.7	57.2	4.6	0.60	2800
Virginia	1.10	38.1	55.1	5.7	0.93	2462
Pennsylvania	.90	39.2	55.2	4.7	1.27	2570
Illinois	6.57	33.51	53.29	6.63	.51	2280
Indiana	11.08	33.27	42.99	12.66	1.47	2320

Size of Fuel. From a practical standpoint it is important that the fuel should be relatively free from fines and should not downgrade under the influence of the abrasion and high blast rates that are now used in the industry in order to secure maximum capacity. The latter requirement is especially important in connection with the use of heavy oils on the fire, as the coke formed tends to clog the fuel bed, particularly in the presence of any considerable amount of small particles.

Characteristics of the Oil—For many years the oil used for making carbureted water gas was known as gas oil and was a fraction in petroleum distillation for which there was very little sale as it was an intermediate between the illuminating oils and the light lubricating oils. This fraction has proved ideal for the manufacture of gasoline so its supply is now very much restricted and the gas industry now uses mixtures of residual oils and residuum from the cracking process. Due to the fact that the oils are generally mixtures, not only of various fractions but also from various fields, the origin of the oil is no longer very helpful in determining its enriching qualities.

Composition and Enriching Efficiency. It appears that, in general, the paraffinic type of hydrocarbons are the most valuable as the ring structure compounds seroiusly reduce the enriching efficiency. The yield of tar is some indication of the undesirability of the aromatic hydrocarbons. In oils composed largely of the paraffinic type of hydrocarbons, the tar will rarely run over 10 per cent of the volume of the oil. With the increasing complexity and the presence of ring compounds, the tar yield will increase up to 15 and 18 per cent, while the residues found in fuel oils may yield up to 30 per cent of tar. The use of a small laboratory apparatus which enables a sample of the oil to be subjected to increasing temperatures in the presence of hydrogen or blue gas has been of great service in predicting the probable usefulness of oil for carbureting purposes, although in most cases a fair estimate may be made of the value of the oil by the use of empirical methods which separate the oil into paraffins, olefines, aromatics, and naphthenes. Table 21 shows the analyses of a number of samples of enriching oils which include both the gas oils, residuums, and fuel oils. In general it may be said that there is fairly good correlation between the hydrogen in the oil and its enriching efficiency: the higher the hydrogen content the greater the efficiency.

TABLE 21—CHARACTERISTICS OF HEAVY FUEL OILS USED FOR ENRICHMENT

Enriching Value 1000's of B.T.U. per Gallon	72.0	80.0	90.3	100.5	111.0
Specific Gravity 60° F.	1.024	1.017	.994	.946	.917
Viscosity Furol	52	272	.....	22	60
Coke per cent by weight	12.2	14.5	13.3	5.3	4.5
Sulfur per cent by weight	0.85	1.77	2.46	0.47	0.51
Distillation:					
Oil to 600° F.	20.5	9.1	24.5	20.4	3.0
600° to 700° F.	54.5	43.3	56.5	42.4	63.9
Empirical Hydrocarbon Analysis:					
Aromatics	20	12	8	12	8
Olefines	34	28	32	8	12
Naphthenes	16	22	12	32	28
Paraffines	30	38	48	48	52

The use of the refractive index of the oil is also of service in predicting its probable efficiency, but in the final analysis, this is essentially a method for indicating the probable percentage of the paraffine or straight chain type of hydrocarbons.

Coke Production. While distillate gas oil usually produces less than 1 per cent of coke, the heavier residual oil will generally contain from 3 to 5 per cent for mid-continent and Gulf coast reduced crudes, to as high as 14 per cent in the heavier Mexican fuel oils.

When the coke yield is above 3 per cent it begins to affect the operation of the carburetor by covering the checker brick with a carbonaceous coating. This coke deposit is apparently quite sticky at one stage in its formation as it collects the ash and fuel dust blown over from the generator and fills up the interstices in the checkering, giving rise to back pressure and poor oil efficiency.

Products of Pyrolysis. The reactions involved in the formation of oil gas have received very extensive study during the past few years with particular reference to the possibility of increasing the production of low-boiling hydrocarbons, such as benzene, toluene, and gasoline. As a result of this study we have acquired a considerable amount of data regarding the general course of the reactions and the most favorable temperatures for emphasizing the production of certain constituents.

In general, the reactions involved follow much the same lines as those occurring during the latter stage of the carbonization of coal. The principal difference is that in the manufacturing of carbureted water gas the temperature and the time of contact are under much more exact control. In this connection, it may be noted that there is a considerably larger ratio of toluene to benzene and a smaller proportion of naphthalene formed than in the manufacture of coal gas.

The products formed with increasing temperatures seem, in general, to follow the reactions that were discussed under the distillation of coal. The illuminants decrease and the hydrogen increases while the paraffines remain about stationary.

TABLE 22—EFFECT OF TEMPERATURE ON DECOMPOSITION OF OIL

Temperature ° *C.*	*Gas per Gal. Cu. Ft.*	*Tar* %	*Coke* %	*Olefines* %	*Paraffines* %	*Hydrogen* %
711	56.4	28.0	1.83	38.0	48.0	11.1
741	61.5	29.4	2.43	33.8	48.3	14.1
751	63.7	26.2	3.63	31.3	50.3	13.5
789	68.0	24.2	3.45	25.0	49.2	19.1
832	80.3	11.9	12.43	13.1	47.0	33.6

The influence of the high partial pressure of hydrogen is especially marked in the formation of carbureted water gas, as the blue gas contains nearly 50 per cent of hydrogen. The hydrogen inhibits the decomposition of the primary products and the splitting off of more hydrogen, which unites with the complex residues, resulting in a higher percentage of olefines, somewhat less gas and more tar. Table 23 shows the composition of oil gas at a given temperature and the calculated and observed mixtures of oil and blue gas.

TABLE 23—CALCULATED AND OBSERVED COMPOSITION OF CARBURETED WATER GAS

	Blue Gas	*Oil Gas*	*Calc. Carb. W. G.*	*Obs. Carb. W. G.*
Illuminants	.0	36.6	9.5	14.8
CO	39.8	1.1	29.7	30.6
H_2	50.0	13.3	40.5	31.4
CH_4	2.2	40.4	12.1	16.8
C_2H_6	.0	6.9	1.8	.3
CO_2	4.6	.5	3.5	3.7
O_2	.4	......	.3	.3
N_2	3.1	1.3	2.6	2.2

Operating Data. Figure 25 gives the data obtained on several types of oil. These data also shows the effect of cracking on the oil efficiency. Figure 26 shows some data exhibiting the effect of varying the amount of oil used and shows the beneficial effect of the high partial pressure of the hydrogen in the blue gas.

With the use of higher fixing temperatures and somewhat smaller quantities of oil per thousand cubic feet of gas, naphthalene stoppages have appeared with carbureted water gas when they were practically unknown under the illuminating value standards.

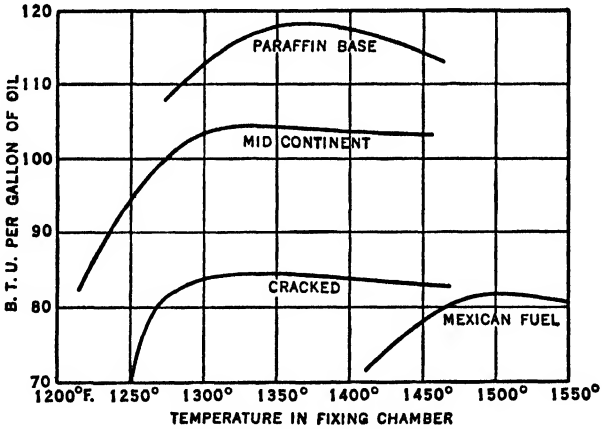

FIG. 25. Effect of Different Oils.

Experiments have indicated that almost the same quantity of naphthalene is made per gallon of oil at the same fixing temperature whether 4 gals. or 2 gals. of oil are used, but with the 4-gal. gas there is nearly three times as much condensate to hold the napthalene in solution. This results in higher concentration of naphthalene in the condensates from the 2-gal. gas and considerably higher naphthalene content in the gas itself. In these tests the 4-gal. gas contains 14 grains naphthalene per 100 cu. ft. and the 2-gal. gas 25 grains per 100 cu. ft.

With some oils the efficient fixing temperatures are so high that naphthalene scrubbing is necessary to prevent stoppages in the distribution system.

Condensation and Purification—The condensation and purification of carbureted water gas follows the same general lines as that previously described for coal gas except that there is no ammonia to be removed. The important impurities are therefore the tar, hydrogen sulfide, and naphthalene. In water gas, however, the gas leaves the wash box at a temperature approximating 190° F. and is frequently nearly saturated with water vapor; at 90 per cent saturation about 86,600 B.T.U. per M.C.F. would have to be removed to bring it to 80° F. so that although the water gas has to be cooled only about 50° F. more than coal gas, the heat to be removed is more than five times as great.

The gas leaving the wash box at a temperature of about 190° F. passes through the scrubbers and primary condensers of either the direct contact or tubular type into the relief holder. The bulk of the tar will now have been deposited. From the relief holder it is drawn by means of the exhausters, and pumped through the secondary condensers and tar extractors.

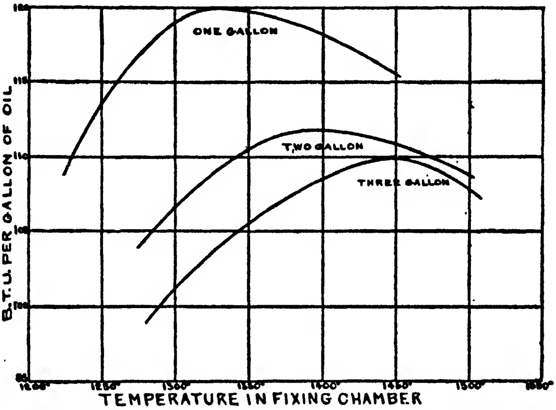

Fig. 26. Effect of Varying Amounts of Oil.

The gas is drawn from the relief holder by means of the exhausters and pumped through the secondary condensers and tar extractors into the purifiers. The tar extractors may be of the P. & A. type or the Cottrell Precipitator.

Due to the fact that there is no ammonia present in the water gas the use of direct contact scrubber condensers is quite general. In this type of condenser the gas is scrubbed with water in a tall grid-filled tower. The water is then cooled in coils and returned to the circulating system.

Purification. The purification of water gas is carried on under the same general conditions as those surrounding the purification of coal gas. The hydrogen sulfide content of water gas will rarely exceed 150 grains per hundred cubic feet so that the work to be done by the purifiers is considerably less than in the case of coal gas. The oxide used frequently contains less iron oxide per bushel than that used for coal gas.

Due to the fact that carbureted water gas is saturated with hydrocarbons, it will carry a certain amount of tar in the form of mist so the water gas oxide becomes contaminated with tar to the point where its efficiency is seriously decreased and the back pressure is increased so that it is rarely possible to secure as high a concentration of sulfur in the oxide as may be obtained in the purification of coal gas.

The use of the Cottrell precipitator for the removal of the last traces of tar has resulted in increasing considerably the capacity of the oxide.

Nitric Oxide. The extraordinary effect of small quantities of nitric oxide in causing the formation of vapor-phase gum deposits in the distribution system has already been discussed in connection with the manufacture of coal gas. The same effect is produced in carbureted water gas. It appears that the source of nitric oxide is the same—that is, it comes from the products of combustion, so the operation of the apparatus must be such that the finished gas will contain a minimum amount of these products. This requires that the products remaining in the set after the blow should be purged by the use of what is frequently called "steam purge" and that the condition of the valves governing the secondary air supplies should be closely controlled. Should these leak during the blow, combustion will take place with a consequent production of nitric oxide. Generally, it is relatively easy to control the operating cycle and conditions so that only a very small amount of the nitric oxide need be produced and this is usually removed in the purification.

Liquid-Phase Gum. The presence of liquid-phase gum in the distribution system is generally indicative of improper condensing facilities. This gum, as its name implies, is formed only in the liquid phase as a result of the polymerization and oxidation of styrene and indene, which must first condense out of the gas as liquids before the gum can form.

In the manufacture of the carbureted water gas, too low a fixing temperature or a very short time of contact of the oil vapors with the fixing vessels may result in the production of an excessive amount of these hydrocarbons; yet it is impossible to operate the process without producing some of them. It is necessary, therefore, to remove them by condensation or scrubbing. In general, this means that the gas should leave the plant with a vapor dewpoint below the lowest temperature to which it may be subjected in the distribution system. This temperature will, of course, vary with the air temperature and must be considered to be lower in the winter than in summer.

If the temperature of the cooling water supply is too high, artificial refrigeration may be used to lower the temperature to the required point. In plants employing naphthalene scrubbers the use of a small additional quantity of oil will generally lower the concentration of the indene and styrene to a point where the gas may be compressed before distribution. The use of suitable after-coolers will generally control the saturation of the gas very satisfactorily.

Specific Gravity of Gas. In order to secure satisfactory service in the combustion of gas in the many complicated appliances now available to the consumer, it is necessary that the specific gravity should be controlled within fairly narrow limits. This is a subject which has only recently received the attention that it deserves. Operating cycles have been perfected which will permit controlling the specific gravity and the use of recording gravitometers has been of great assistance.

OIL GAS

The manufacture of oil gas as practiced on the Pacific coast is related in a general way to the manufacture of water gas. Essentially, it is a cracking process whereby the oil is in part broken down to its constituent hydrogen, and lampblack and the remainder is left as permanent gas with relatively small amounts of vapor so that its composition closely resembles coal gas. This process is an excellent example of the adaptation of means to utilize the existing raw materials more efficiently. In general bituminous coal and coke are expensive on the Pacific coast due to the long distances they have to be transported, whereas an abundant supply of rather cheap oil is readily available. Therefore, the manufacture of oil gas has been the logical solution.

Because of extension in the use of natural gas, however, many cities formerly using large quantities of oil gas have changed over to natural gas within the last decade.

Methods of Operation—There are two distinct methods of operating. One method attempts to make the minimum amount of lampblack and is typified by the Jones apparatus, while the other method deliberately attempts to make a considerable quantity of lampblack, using more oil, of course, but putting the lampblack into marketable form with the idea that as a by-product it is more valuable than the original oil. Evidently, local conditions must determine the relative efficiencies of these processes.

Jones Apparatus. In the Jones type of apparatus, a set with a capacity of 5,000,000 cu. ft. per day has shells which are 18 ft. 9 in. outside diameter lined to 14 ft. 3 in. diameter. The primary shell is 49 ft. high while the secondary is 63 ft. high; the connection being 10 ft. by 17 ft.

In operation, air is blown into the primary shell for 3 minutes, to burn out the carbon, then for 2 minutes it is also blown into the base of the secondary shell. The second blast is shut down and oil is turned on in the top of the primary for 5 minutes. The temperature in the primary checker will now be between 1600° and 1700° F. and in the secondary about 100° F. lower. The oil and blast are shut off and steam is turned on the top of the primary and the secondary for 1 minute. During this time blue water gas is made. Oil is then turned into the lower checker brick in the primary and into upper checkers in the secondary for 7 minutes. The oil is then cut off and steam alone used for 2 minutes, which completes the cycle. The oil is sprayed into the machines with steam and must be preheated to give it the necessary fluidity.

The temperatures are controlled by pyrometers and are checked by the appearance of the overflow at the wash box. In making gas of 550 B.T.U. per cubic foot about 7.0 gals. of oil per thousand cubic feet are required. About 1.0 gal. is used during the heating period, the remainder during the making period.

The gas will have the following composition and characteristics when made from heavy California crude.

	Per Cent
Ills.	4.2
CO	10.4
H_2	47.6
CH_4	27.0
CO_2	4.6
O_2	.4
N_2	5.8
Sp. gr.	.476
B.T.U.	554

About 12 lbs. of lampblack and 0.5 gal. of tar will be produced per one thousand cubic feet of gas.

Alternate Apparatus. The other type of apparatus is known as the straight, short set and consists of a single shell divided into sections by arches which carry the checker brick. The top is provided with a stack valve. In a set with a capacity of 2,400,000 cubic feet per day, the shell would be 20 ft. diameter lined to 17 ft. by 36 ft. high. The blast chamber and heating burners are at the base. The wash box is 8 ft. diameter and 7 ft. high.

The operation is, in general, the same as previously described, but the cycles are usually 10 minutes heating and 20 minutes making, and for a 550 B.T.U. gas the oil per thousand would be about 8.6 gals. per thousand cubic feet and there would be provided about 23 lbs. of lampblack and .2 gal. of tar.

The gas will have practically the same composition as that made in the other process. In comparing the heating value put into the gas per gallon of make oil used in the oil gas process with the carbureted water gas process, we would get the following figures.

Straight shot	23 lbs. carbon	.2 gal. tar	7,250 B.T.U. per gal.
Jones	12 " "	.5 " "	87,700 " " "
Carbureted water gas	None	.5 " "	105,700 " " "

The straight-shot apparatus can be operated in the same manner as the Jones set—i.e., with a minimum production of lampblack and will give nearly the same oil efficiencies on equivalent sizes of apparatus.

In the early days of this process the working conditions were not well understood and the operation of the machines resulted in enormous accumulation of lampblack from excessive and irregular temperatures carried in the apparatus. Now, however, with the control that is exercised over the operation of the set, in addition to the better design, the apparatus has resulted in an almost total elimination of the trouble and nuisance due to lampblack. The bulk of the lampblack is now removed in a self-cleaning wash box in which it is washed from the gas by a large quantity of water, which prevents the formation of large lumps.

Scrubbing. From the wash box the gas passes through scrubbers filled with wooden trays similar to those used in the carbureted water gas apparatus. As there are no by-products to be saved, a rather excessive amount of water is supplied to the scrubbers. In some of the plants three scrubbers are used, applying from 10 to 15 gals. per thousand cubic feet per scrubber, or a total of, say, 40 gals. per thousand cubic feet. The water from the wash box and scrubbers is run into the lampblack separator, where the lampblack is removed. The lampblack as taken from the separator contains about 60 per cent of water. This is piled in heaps and allowed to drain until it contains about 20 per cent. It is then used for fuel either under the boilers or in water gas apparatus.

In some of the more modern plants the lampblack is removed from the wash-box water by vacuum filters, is dried in rotary oil-fired driers and is then briquetted.

Due to the high temperatures employed in the fixing chambers, a considerable quantity of naphthalene is formed. This is removed by scrubbing the gas as it leaves the last water scrubbers with the oil used for gas making. About 5 gals. per thousand cubic feet is used in grid-filled scrubbers.

A great advantage of this type of apparatus is that it can be built and handled in large units, so that the operative labor is reduced to a minimum, and no time is lost in clinkering. The machines can be depended upon to produce their gas continuously, so only a very low holder capacity is required.

Condensation and Purification—The condensation and purification of the gas follow very closely the practice previously described under carbureted water gas, except that the removal of the last traces of lampblack and the small quantities of tar require special consideration. The hydrogen sulfide is usually low.

Type of Oil—Of the available oils in California, it has been found that those of highest specific gravity give the best results or, in other words, that the hydrocarbons present in the oil are all about equally valuable, so that the oil yielding the greatest weight per gallon will naturally give the greatest number of cubic feet of gas. This result rather bears out the idea that has been gaining ground in the East where the heavier grades of enriching oil have been tried out and experimented with more thoroughly. The heavier grades of oil require heating so that they will spray properly. The sulfur content of the California oils varies quite widely, some crudes containing as much as 4 per cent. It has been found that where the sulfur does not exceed 1 per cent, the gas is readily purified with iron oxide, as the hydrogen sulfide will not exceed 300 grains per 100 cubic feet.

With some oils the organic sulfur has given considerable trouble and this led to the use of the Hall reheating process for the removal of the organic sulfur compounds.

GENERAL PROCESSES AND OPERATIONS

Heretofore we have considered only the manufacture and purification of the several commercial gases, as these processes have differed considerably for each class. We will now take up several steps that, while they more properly belong to the distribution of the gas, they are undertaken at the plant and may now be briefly considered here as being common to all the various classes.

Metering—After the gas passes the purifier it is metered in order that a proper check may be kept upon manufacturing operations. The volume of gas made is usually corrected to 60° F. and 30″ mercury.

Until recently the wet drum meter which operates by the displacement of a water-sealer drum was the standard form of apparatus used in the metering of manufactured gas. Where large volumes of gas have to be handled this type of meter becomes very bulky and expensive and it has been replaced by the so-called rotary meter which is in effect a small positive blower provided with a recording mechanism and which is operated by the gas pressure. A meter of this type is shown in Figure 27. This type of meter is much more compact, occupies but little room and is considerably cheaper both in first cost and in maintenance.

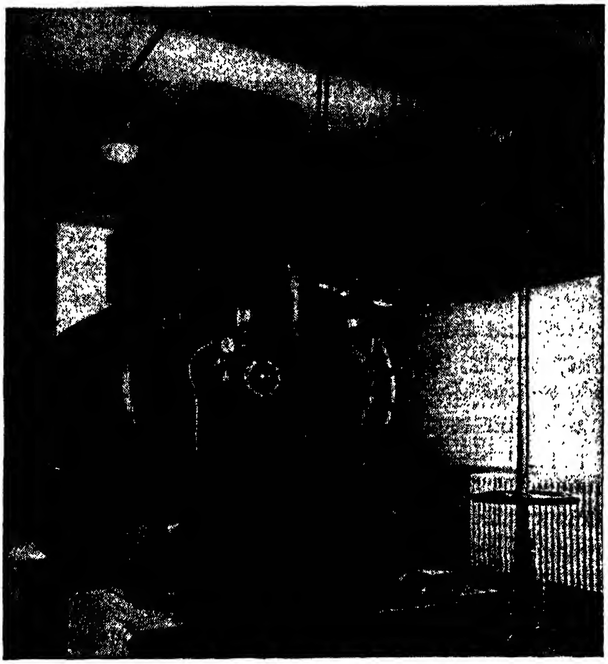

Fig. 27. Low Pressure Meter; Displacement 65.28 CFR; Maximum Continuous Hourly Rating 910,000 CFH.

An electric meter has been used which automatically records the mass and therefore the volume at a definite temperature of the gas by the rise in temperature of the stream of gas that has had a definite quantity of heat added to it electrically. Actually the rise in temperature is maintained constant and the varying amounts of energy necessary to maintain this rise are recorded and then related directly to the mass of gas delivered.

In large installations, particularly in the coke-oven industry, where large volumes of gas have to be measured and absolute accuracy is not required, Venturi meters with an automatic integrating mechanism have been used. These have been successfully employed where the flow is fairly uniform and their use was desirable owing to low installation cost.

Holders—From the meters the purified gas passes to the storage holders (see Figure 1). The holder proper, or bell, is built of thin sheet iron or mild steel, supported in a structural steel guide-frame. The holder, if large, is composed of several sections to reduce the depth of the tank in which it is sealed. The various sections are joined with water seals which, in climates where freezing weather is prevalent, must be heated to prevent the water from freezing and thus damaging the holder. The tanks are either of brick or concrete, built in the ground, or of steel above the ground. Owing to the great weight of the water and steel composing the holder the foundation must be carefully prepared, especially where the tank is of brick or concrete.

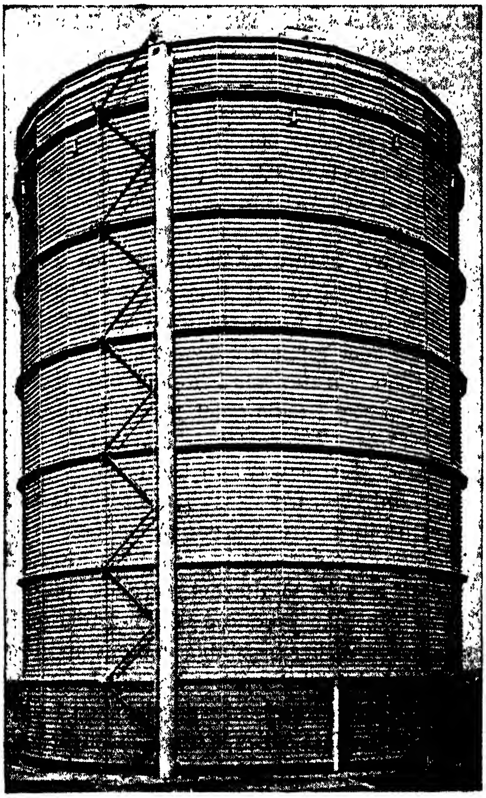

FIG. 28. Waterless Gas Holder, Capacity 15,000,000 Cubic Feet. (Courtesy Consolidated Edison Co. of New York)

Waterless Holders. Within recent years another type of storage holder has been introduced which is known as the waterless type. The holder proper is so fabricated that the interior is smooth and serves as a cylinder for a piston, which rises and falls in response to the volume of gas in the holder (Figure 28).

The joint between the piston and the body of the holder proper is made by means of a set of steel shoes rubbing against the side of the holder and connected to the body of the piston proper by heavy canvas.

This joint is built in the form of a cup below the top of the piston proper and this cup is filled with a heavy oil or tar of sufficient depth to resist the pressure of the gas in the holder. Provision is made for catching any oil which may leak through the joint to the base of the holder and returning it by means of automatic pumps to the top of the piston.

In another form of construction the piston has a number of packing rings and a grease is used to lubricate the joint and to render it gas-tight. This type of holder eliminates the operation cost of the pumps that are required where tar or oil is used as a seal. The waterless type of holder lends itself especially well to situations where foundation conditions are not of the best.

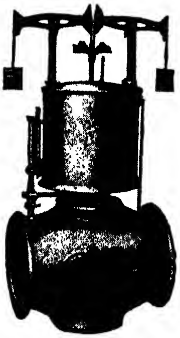

Fig. 29. The Connelly Type M. S. Mercury Gas Governor Delivers Constant Outlet Pressure in Direct Proportion to the Volume.

Station Governors. In order to secure proper and adequate pressure conditions, the gas as it passes out of the holders is fed through governors which automatically maintain a constant pressure, or in some cases increase and decrease the pressure in accordance with the varying rate of flow. Figure 29 illustrates one form.

Utilization of Residuals—The residuals or by-products depend upon the kind of gas made. Coal gas gives coke, coal tar, ammonia, cyanogen, spent oxide and retort carbon. Water gas has only one, the tar, while the all-oil gas of the Pacific coast yields lampblack.

Coke. The retort coke is usually crushed, the breeze or fine dust removed and the crushed product separated into several sizes for sale. The breeze is usually burned at the plant in the producers or as boiler fuel either alone on specially-constructed grates with forced draft or mixed with coal, or sold as filtering material.

The coke produced in the ordinary horizontal retorts is generally of small size, has a rather high bulk content and low crushing strength. While this is satisfactory for domestic use it has not been used for foundry purposes. The coke made in by-product coke plants, even from high volatile coals, and the coke made in the vertical ovens is much stronger and is satisfactory for use for foundry purposes.

The lampblack is allowed to drain and air dry and may be used directly as boiler fuel, but successful results have lately been obtained by briquetting the dried material, there being sufficient tar present to act as a binder.

The retort carbon is sold as such and is used in the manufacture of arc and battery carbons, dry batteries and other purposes requiring a hard, dense form of carbon.

Tar. The tars are generally sold to tar distillers after the water content has been reduced to 3 per cent, which is the usual basis of sale.

The water-gas tar produced with certain oils frequently gives considerable trouble due to the formation of emulsions which may contain as high as 90 per cent water. This phenomenon occurs only occasionally with distillate oils, but where the heavier fuel oils are used the tar will rarely contain less than 50 per cent of water, so that the removal of this water at times presents quite a serious problem.

A considerable amount of research work has been done which indicates that the formation of emulsion is due to a tough coating of oily material around each of the particles of water which is difficult to disrupt. A number of processes have been developed to overcome the trouble. Among these may be mentioned the heating of the material under pressure above the boiling point of water. In many cases this apparently will break the enclosing envelope, thus permitting the water globules to coalesce and separate from the tar. The use of centrifugal apparatus is generally satisfactory for breaking the emulsion, but the capacity is low because of the presence of a small amount of coke breeze and other material in the tar, which requires very frequent cleaning of the rotor. In cases of persistent emulsions it has been found necessary at times actually to distill off all of the water in the form of steam. This is, of course, time consuming and requires the expenditure of a large amount of heat. It has recently been proposed to heat the emulsion under pressure to a relatively high temperature in a pipe still and then allow it to flash off in an evaporator similar to that used in the distillation of petroleum.

Few plants attempt to refine their tar. In many of the smaller plants and where freight rates are unfavorable or other conditions do not permit shipping the crude tar to a distiller, the tar is burned as fuel under the benches or boilers. The heating value of the tars will range from 15,000 to 18,000 B.T.U. per pound.

BY-PRODUCTS

Light-Oil Recovery—While light-oil recovery has been generally practiced in connection with coke ovens it was not until the demand for toluene brought about by the first World War became so insistent that light-oil recovery plants were introduced into city-gas plants. About twenty-two plants were erected, but at the present time only three or four plants are operating and these plants are producing a refined light oil for use as motor fuel, generally in admixture with an equal volume of gasoline.

TABLE 24—LIGHT-OIL YIELDS

	Horizontal Retorts	*Vertical Retorts*	*Coke Ovens*	*Carb. Water Gas*	*All-oil Water Gas*
	Gal./Ton	*Gal./Ton*	*Gal./Ton*	*Per Cent*	*Per Cent*
C.P. benzol	1.62	1.81	1.782	4.5	3.3
C.P. toluol	.41	.43	.402	2.2	.2
Refined naphthas	.30	.41	.216	1.0	.03
Unsaturated hydrocarbons	.36	.43	.297	3.1	.60
	2.69	3.08	2.707	10.8	4.13

The most important source of light oil is the by-product coke-oven industry. The majority of the coke ovens are provided with light-oil recovery plants.

The amounts and relative proportions of the condensable hydrocarbons present in city gas varies considerably with the process, i.e., coal-carbureted water gas, all-oil water gas; and with the type of apparatus; and with the raw materials.

In discussing the quantities involved it has been thought more logical to express them in gallons per ton of coal carbonized for coal gas and as a percentage of the gas oil used for carbureted water gas.

In this connection the use of "C.P." and "refined" indicates that the hydrocarbons were washed with acid and soda before valuation.

Method of Recovery—The method of recovery in general use involves scrubbing or washing the gas with an oil of high boiling point (low vapor tension) until it has absorbed from 2.5 to 3.0 per cent of the light hydrocarbons. The so-called benzolized oil is then heated to 240° to 280° F. and distilled with live steam, thus liberating the low-boiling benzol homologs. The debenzolized wash oil is then cooled by heat exchangers and water coolers and is returned to the cycle.

It is evident that given a wash oil of low vapor tension, the extraction will depend upon the relative amount of low-boiling vapors present, the saturation of the benzolized wash oil, i.e., the volume of wash oil per unit volume of gas, and the temperature. As the temperature increases, the volume of wash oil must be increased to decrease the percentage of saturation to obtain equal efficiency of extraction. The highest commercial efficiency of extraction is between 92 to 95 per cent, while average working will probably not exceed 90 per cent. The wash oil used is generally a high-boiling petroleum oil known as "absorbent" or "straw oil."

Operation—The recovery apparatus is usually installed in coal-gas plants after the ammonia washers where the gas has already been cooled and the temperature for the highest extraction is rarely allowed to exceed 75° F. In water-gas plants it is usually installed after the purifiers.

While the main features of the recovery apparatus is the same in nearly all the modern systems there are a number of minor points of difference, principally in design.

Here the gas is brought into contact with the wash oil in two tall towers filled with layers of boards on edge or ceramic forms in order to break up the gas stream and to expose the maximum surface of oil to the gas. The oil is sprayed down the towers against the rising stream of gas. Separators similar to steam separators in the gas outlet pipes prevent the loss of wash oil in the form of the mist or spray while the bottom of the towers and external separators remove any water that is deposited out from the gas. The wash oil now contains from 2.5 to 3.0 per cent of crude benzol and is at a temperature of, say, 75° F.

It then passes to a vapor to oil heat exchanger where it is heated to 150° F. by the latent heat of the vapors from the debenzolizing still, then through an oil-to-oil heat exchanger where it is heated to 220° F. by the hot wash oil from the bottom of the still, thence to the steam preheater where high-pressure steam is used to bring the temperatures up to 270° to 290° F.

Distillation. It is essential that the oil be brought to a high temperature before it enters the still. The hot oil now passes down the column of the debenzolizing still. This is composed of cast-iron sections of the same general principle as that shown in detail in Figure 30 but having somewhat larger run-back passages.

Usually there are 8 or 10 sections at the top of the column, of a smaller sectional area than the 14 to 18 sections at the bottom, through which the oil flows. At the base of the column is a spray through which live steam is introduced equal in amount to 70 to 100 per cent of the volume of crude benzols distilled out.

As the steam rises through the current of descending hot oil the low-boiling vapors are liberated and rise through the column, thus thoroughly scrubbing the incoming oil and depositing the considerable quantity of the wash oil that is carried forward mechanically in the upper sections. A certain amount of the wash oil, however, comes over with the crude benzols and may run as high as 20 per cent by volume, although good working condition will reduce this to from 3 to 8 per cent.

The vapors then pass to the vapor-oil heat exchanger, where they give up most of their latent heat to the incoming benzolized wash oil, then to condensers, and finally to a separator to remove the condensed steam and to the storage tanks.

The debenzolized wash oil leaves the base of the column at about 240° F. and passes through the oil-to-oil heat exchanger, thus heating the incoming benzolized wash oil and cooling to about 170° F.; from here it passes to the coolers which are usually of the ammonia type where it is cooled to 75° F., and then passes to the debenzolized wash oil tank and is ready to commence the cycle again.

In order to secure maximum recovery of the light oil, vacuum stills have been used.

In other systems the tower scrubbers are replaced with mechanical scrubbers, or in one system with a column similar to that used in the debenzolizing still. In the operation of recovery apparatus the quantity of recoverable hydrocarbons present, the gas temperature, and the efficiency of recovery desired are determining factors.

Efficiency of Recovery—In coke-oven plants where complete recovery is the goal, the temperatures are usually held below 75° F., and sufficient wash oil is used to yield saturation of the benzolized oil of not over 2½ per cent, i.e., at 2.0 gals. of light oil per ton of coal and 10,800 cu. ft. per ton, this would mean 7.22 gals. of wash oil per 1000 cu. ft. With higher temperatures and greater quantities of light oils present, the wash oil used may run up to 14 to 16 gals. per 1000 cu. ft.

The practically complete elimination of the light oil from the benzolized oil is important in securing high recovery efficiencies. To a great extent this is secured by a uniformly high temperature of the oil entering the debenzolizing column. It is difficult to secure complete elimination of light oil with a temperature less than 220° F., and this will require considerably more live steam than where the oil is from 240° to 280° F., at which temperatures the recovery is complete and the whole operation is much more smooth and uniform. The live steam required varies from 70 to 100 per cent by volume of the light oil produced.

The light oil is generally sold to tar refiners, although a few of the coke-oven companies refine the light oil directly at the plants.

Cyanogen—When coal gas is produced in horizontal retorts there is a considerable production of cyanogen. At one time several of the larger plants installed processes for the recovery of cyanogen in the form of an insoluble ferro ferricyanide of ammonia. In the coke-oven plants, however, the amount of cyanogen is quite low and, due to the fact that liquid purification processes usually remove nearly all of the cyanogen, its recovery from manufactured gas has been generally discontinued.

The spent oxide from coal-gas plants where the cyanogen is not extracted will contain practically all the cyanogen from the gas as Prussian blue together with some ammonium salts. In the ordinary oxide the Prussian blue will range from 7 to 13 per cent; it thus becomes available as a source of cyanogen and is sold as such.

Ammonia—The ammonia which is recovered as condensate and as a weak liquor in the ammonia scrubbers will average from 1 to 2 per cent by weight and exists principally as an acid carbonate and chloride together with small quantities of a number of other ammonia compounds.

Due to the development of synthetic processes for the manufacture of ammonia, the ammonia liquor produced in gas plants is no longer a valuable by-product and in most cases the price received is so small that it will not pay to transport the weak liquor. A few of the plants having sufficient production concentrate the liquor up to a strength of 20 to 25 per cent, which is known as "B liquor." This process is carried on in ammonia stills.

Recovery Methods. The ammonia occurs in two forms: as ammonia, ammonium carbonate, and ammonium hydrosulfide, in which form it can be set free by the application of heat; and as fixed ammonia salts, sulfate, cyanide, etc., which require the addition of an alkali to set the ammonia free.

The ammonia gas and steam are driven off through towers, similar to the dephlegmator towers in use in the distillation of benzol, etc., and then passes to a water-cooled condenser where the concentrated ammonia is collected. In the practical operation of the plant the liquor is analyzed for the proportion of free and fixed salts and a proper amount of milk of lime is added.

Considerable care and experience are necessary in the operation of the stills in order to produce a marketable grade of B liquor. Stipulations are fairly strict as to the proportion of hydrogen sulfide and carbon dioxide that may remain in the liquor and the color must be carefully controlled.

In many plants only the volatile ammonia, which is by far the greater percentage, is recovered and the fixed ammonia is allowed to go to waste.

Ammonium Sulfate. The manufacture of ammonium sulfate by the direct process has already been touched on. In the indirect process the operation is practically a combination of the concentrating apparatus, as far as the stills are concerned, where the liquor is freed from the ammonia. The vapors, instead of being condensed to a concentrated liquor, are passed into the lead-lined saturator box where they are brought in contact with the sulfuric acid.

The ammonium sulfate, as it forms in the saturator, is fished out, allowed to drain, and is usually freed from excess moisture in the centrifugal. The manufacture of ammonium sulfate is confined almost entirely to the coke ovens.

Products from Sulfur—Normally the presence of shavings in the spent oxide, together with tar, prevents its use for the manufacture of sulfuric acid. Some experiments have been made, however, using blast furnace slag as the distending agent. If this is used and Cottrell precipitators, or other efficient forms of tar-removing apparatus are employed, it has been claimed that some plants have been able to sell their spent oxide for acid manufacture.

The use of liquid purification processes for hydrogen sulfide removal have resulted in several new by-products. In the Thylox system the finely divided sulfur that is recovered has found a certain use as a fungicide and in the preparation of sprays for agricultural purposes. It has also been melted and cast into bricks and burned in the manufacture of sulfuric acid. Sodium thiosulfide and thiocyanate have been separated by fractional crystallization.

In some cases ammonia has been used instead of sodium in the Thylox process and this gives rise to a rather valuable by-product in the form of ammonium thiocyanate which has a number of chemical uses. It can, for example, be transformed into thiourea by heating under proper conditions.

CHAPTER 16

COAL TAR AND ITS DISTILLATION PRODUCTS

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SOURCES OF TAR

Tar is the black, foul-smelling, oily mixture which separates from the gases formed in the destructive distillation of coal. The raw tar is composed of light oils, pyridine bases, phenols, naphthalene, anthracene, heavy oils, pitch, complex organic compounds insoluble in benzene, known as free carbon, water, ammonia, and dissolved constituents of the gas. It is the raw material from which benzene, toluene, xylene, solvent naphthas, phenol, cresols, naphthalene, anthracene, pyridine bases and numerous other compounds are obtained. As there is little prospect that the principal object of the destructive distillation of coal will be the production of tar, there has been little research upon the conditions necessary to produce tar of the most desirable properties. It varies greatly in composition and may be divided into retort gas tar and oven gas tar, etc., according to its method of production.

Retort Gas Tar—This tar is obtained as a condensation product in the hydraulic mains, scrubbers, or condensers, in the manufacture of coal gas for illuminating purposes. It is less fluid and contains less of the lighter hydrocarbons, more naphthalene, anthracene and their accompanying oils, and more free carbon than tars from some other sources. The composition varies with the heats and coals employed. The lower the carbonization temperature of any coal, the more fluid the tar and the lower the free carbon content.

The specific gravity of the dry (water-free) tar varies from 1.10 to 1.25 or even somewhat higher.

It contains from 18 to 40 per cent of free carbon and yields on distillation from 1 to 5 per cent of light oil to about 200° C., 30 to 50 per cent heavy oil, including naphthalene, anthracene, phenols, and accompanying oils, from 200° C. to the coking temperature, and from 45 to 65 per cent coke; or if distilled to pitch, the yield would be light oil 1 to 5 per cent, heavy oil 25 to 40 per cent, and pitch 50 to 75 per cent.

Oven Gas Tar—This material is obtained as a by-product in the distillation of coal in retort coke ovens. It is similar to retort gas tar, except that it is more fluid. It contains more of the hydrocarbons, and considerably less free carbon, which latter usually runs from 5 to 20 per cent.

The composition of course changes with the coal, with type of oven, and with the coking temperature.

Low Temperature Tar—It seems to be certain that marketable quantities of tar from low temperature carbonization of coal will be produced in the near future. These tars are usually distinguished by a specific gravity but slightly greater than water, low free carbon content and a much higher percentage of oils than the other varieties of coal tar. The oils are of low specific gravity and largely parafinoid compounds instead of those of the aromatic series. They also contain large percentages of tar acids similar to those of blast furnace tar.

Producer Gas Tar—Owing to the method of production this usually consists of large percentages of water and free carbon together with a very small amount of oils, and yields, when distilled, a very friable pitch entirely unsuitable for the purposes for which pitch is made and therefore of no commercial importance.

Blast Furnace Tar—This is essentially a low heat tar, being produced in blast furnaces fed with coal instead of coke. It usually has a specific gravity between 0.94 and 1.000 and contains more phenoloid and basic substances than ordinary coal tar. These phenoloid substances resemble those obtained from the destructive distillation of wood and lignite and amount to from 5 to 10 per cent of the tar, while 1 to 2 per cent is the usual amount in ordinary coal tar.

It also contains from 2 to 5 per cent of basic bodies and about 16 per cent of paraffin oils which solidify in cooling. These tars are entirely different from the ordinary coal tar and not suited for the same purposes.

Water Gas Tar—From the manufacture of carburetted water gas for illuminating purposes, the tar obtained differs mainly from the others in the entire absence of tar acids (the phenol group), ammoniacal liquor, and in the small amount of free carbon present, which is usually less than 2 per cent in these tars.

The specific gravity varies from 1.005 to 1.15, but is usually between 1.03 and 1.12 in tars from the larger and more carefully supervised works.

Dry water gas tar, when distilled, yields from 5 to 15 per cent of light oil to 200° C., 30 to 50 per cent of heavy oil from 200° C. to pitch, and 35 to 60 per cent of pitch.

EFFECT OF CARBONIZATION TEMPERATURE ON TAR COMPOSITION

The effect of variations in the carbonizing temperature upon a coking coal in ordinary gas retorts is shown by the typical data in Table 1.

TABLE 1—EFFECTS OF VARIATIONS IN CARBONIZING TEMPERATURE

	600° C.	*650° C.*	*700° C.*	*750° C.*	*800° C.*
Cubic feet of gas per ton of coal	6,600	7,200	8,900	10,162	11,700
Specific gravity of the tar	1.086	1.120	1.140	1.154	1.206
Composition of the tar percentage by weight:					
Ammonia liquor	1.20	1.03	1.04	1.05	0.383
Crude naphtha	9.17	9.65	3.73	3.45	0.995
Light oil	10.50	7.46	4.47	2.59	0.567
Creosote oil	26.45	25.83	27.29	27.33	19.440
Anthracene oil	20.32	15.57	18.13	13.77	12.280
Pitch	28.89	36.80	41.80	47.67	64.080
Total	96.53	96.34	96.46	95.86	97.745

These data show not only the increased yield of gas but also the loss of the valuable light constituents of the tar and the increase in bitumens with the increase in temperature.

As these studies were conducted in ordinary horizontal gas works retorts, the primary products of the carbonization of the coal were in contact with the hot walls of the retort for an appreciable time and therefore were cracked more than would be expected by the temperature.

The composition of the tar from the 600° C. temperature corresponds closely to that from vertical retorts; those from 650° C. and 700° C. are quite similar to coke oven tars; that from 800° C. to tar obtained in modern horizontal retort operation.

Tars from the carbonization of coal at low temperatures, or where the volatile products are removed, without being subjected to a cracking process by passing through a hot zone, are quite different from the usual coal tar. They are usually lower in specific gravity, and consist of paraffin oils instead of those of the benzol series.

Physical Properties of Different Tars—Table 2 shows the variations of the physical properties of coal tar due to the kind of apparatus used to carbonize the coal.

TABLE 2—PHYSICAL PROPERTIES OF COAL TARS

	Retort Gas Tar		*Oven Gas Tar*	
	Horizontal Retort	*Vertical Retort*	*Slot Oven*	*Sole Flue Oven*
Specific gravity at 15.5° C.	1.24-1.30	1.13-1.16	1.10-1.25	1.085-1.110
Viscosity (Engler) 100 c.c. at 100° C.	Sec. 160-640	Sec. 40-45	Sec. 40-95	.....
Free carbon or insoluble in benzol-toluol	20-40%	2-6%	4-15%	2-6%
Unsulphonated residue	.....	0-5%	0-5%	.....
Light oil to 210° C., per cent by volume	1-3.5	2-10	0.5-4	6.7-15
Middle oil, heavy oil and anthracene oil, 210° C.-355° C., per cent by volume	25-30	40-45	30-55	55-62
Total oil to pitch, 140° F.-M.P., per cent by volume	13-20	26-29	15-39	(about) 50
Total oil to 200° F.-M.P. pitch, per cent by volume	18-23	(about) 37	29-40	50-60

USES OF TAR

Tar, like petroleum, is a very complicated substance and contains literally thousands of different compounds, many of them valuable in various other chemical industries. As a matter of fact early organic chemical industries, particularly synthetic dyes, depended almost entirely on coal tar for raw materials.[1] However, only a small proportion of the tar is ordinarily used to recover the chemicals used for solvents or synthesis because the supply far exceeds the demand in this field. This is largely due to the advent of an increasing number of by-product coke ovens for manufactured gas. Hence, it is a very inexpensive source of raw materials.

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[1] See Chapter 27, Table 7, and Chapter 28.

The distribution of uses of tar depends to a great extent upon economic conditions, but ordinarily it is plentiful and inexpensive enough in the United States to be used as fuel. Ordinarily, a large amount goes for this purpose. Outside of its application as fuel, tar is little used in the crude state, but is refined by removing the water and more or less oil by distillation. In this condition it is used to saturate roofing felt, to coat roofs laid with plain tarred felt, as a cheap paint, and to coat wood which is to be buried in the ground. With more oil removed it is used as a binder in asphalt pavements and tar-macadam roads. With an admixture of water, it is used to sprinkle Telford and macadam roads to prevent dust.

The materials recovered by the refining processes have a variety of uses which will be pointed out in the discussion on methods of recovery.

Distribution of Uses—The distribution of uses in recent decades is shown in Table 3.

TABLE 3—PRODUCTION OF TARS IN UNITED STATES IN GALLONS

	1900	*1920*	*1927*	*1939*
Coal tar	21,680,000	411,929,080	599,052,000	554,406,280
Water-gas tar	82,186,314	116,073,907	82,528,822	141,440,000
Coal tar burned	None	189,163,718	139,634,166	157,024,124
Coal tar sold	22,064,600	22,765,362	459,417,834	344,534,382

Most of the coal tar burned is used with producer gas to heat open hearth furnaces for the production of steel. The incandescent carbon of the burning tar facilitates the regulation of the flame and increases the rapidity of the melting process.

The average price per gallon of the coal tar sold has increased steadily from 2.5¢ in 1900 to 1910 to 5.2¢ in 1927 and 4.9¢ in 1939.

Exports and Imports—There has been a considerable increase in the exports of tar and in the imports as reported by the U. S. Department of Commerce and shown in Table 4.

TABLE 4—U. S. EXPORTS AND IMPORTS OF TAR

	1910	*1920*	*1927*	*1939*
Coal tar exports, barrels	110,523	88,350	673,419	177,454
Coal tar imports, barrels	35,658	11,901	12,951	79,630

From the above statistics it will be seen that there has been a very large expansion in the industry in the last 40 years.

PURIFICATION OF TARS

Tars are separated into their valuable constituents by simple distillation. The stills, Figures 1 and 2, may be either horizontal or vertical cylinders set in brick work and heated by direct fire similar to steam boilers. They vary in size and in design. Those with a capacity of 10,000 gallons are not uncommon, but most stills have less than half this capacity. The European practice is to use vertical stills with convex top and concave bottoms.

The top and sides are constructed of half-inch boiler plate, while the bottoms are frequently from 1 to 1¼ ins. in thickness and are protected from the direct heat of the fire by a brick arch. The hot gases from the fire are led around the lower half of the still in flues.

The American practice is to use horizontal stills heated on slightly less than half of their cylindrical surface and protected by an arch directly over the fire and so designed that the portion of the shell heated may be readily replaced when damaged. The still is equipped with the usual worm, to act as a condenser, which may be made of either cast- or wrought-iron pipe, with receivers, and with a pitch cooler. The objections to cast-iron worms are their numerous joints and great weight. Since the development of electric welding, wrought-iron worms may be made of any desired length with no joints to give trouble. Where high-carbon tars are worked, stills must be provided with suitable means of agitating to prevent the carbon becoming caked upon the heated part of the shell. Drag chains were formerly employed for this purpose, but compressed air or superheated steam are now more often used, as they serve to keep the still clean and to assist in removing the high-boiling oils.

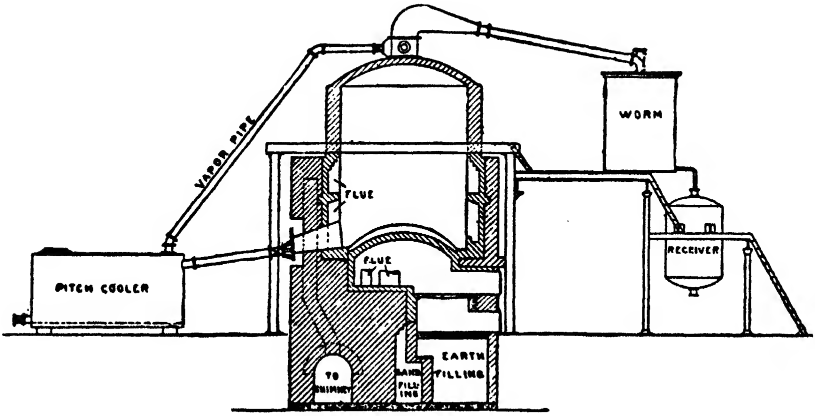

FIG. 1. European Tar Still.

Continuous stills to which is fed a constant stream of tar and from which the separated fractions and pitch flow in steady streams have been tried in numerous designs, but their cost and supervision have held back their use.

TABLE 5—COMPARISONS OF FRACTIONATIONS IN AMERICAN AND EUROPEAN PRACTICE

American Practice

Light oil, or Crude naptha	Till oil sinks in water, about 200° C.
Heavy oil, Dead oil, or Creosote oil	200° C. to pitch
Pitch	Residuum

European Practice

First light oil, or First runnings	To 110° C.
Light oil, or Second light oil	110° to 200° C.
Carbolic oil	200° to 240° C.
Creosote oil	240° to 270° C.
Anthracene oil	270° C. to pitch
Pitch	Residuum

Character of Fractionations—Since the stills are operated batchwise, the different fractions in the cycle are markedly different. The operation of tar stills varies considerably at different works. The receivers are changed at different temperatures and therefore the products are not uniform. In America it is the more common practice to take the first fraction as light oil until the distillate commences to sink in water, and as heavy oil or creosote oil from that point to pitch. Very little, if any, anthracene is made in this country, as most of the tar is run only to soft pitch with a melting-point between 60 and 80° C.

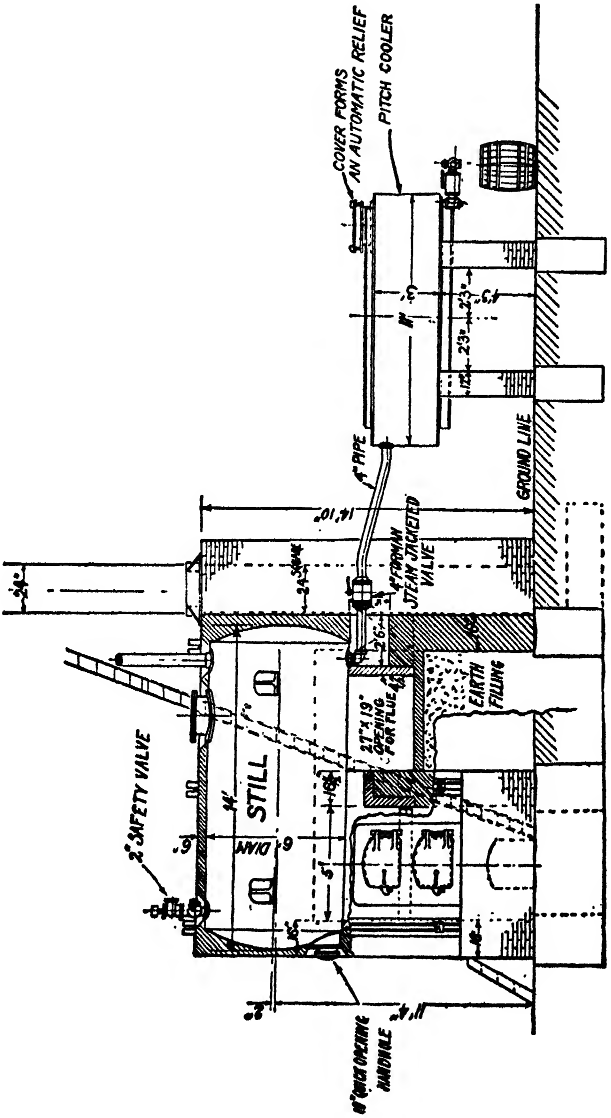

Fig. 2. American Tar Still.

The European practice is different. From four to six fractions are taken before the pitch and a very large percentage of the tar is run to hard pitch. Table 5 shows the most common fractions and the temperatures of the "cuts."

In the American refineries during the last few years there has been more or less tendency to divide the creosote oil fraction into carbolic oil and heavy oil by a cut at about 240° C. in order to recover the tar acids.

General Operation of Stills—The tar is usually charged into the still while it is still hot from a previous run. The fire is lighted when the charging is about half completed. It must be carefully regulated until the rumbling or crackling noise in the still ceases, which denotes that the water has all been driven over. The firing can now be pushed so that the distillate runs at the rate of 200 to 400 gallons per hour. When the desired grade of pitch has been obtained, the fire is drawn and the pitch is run or drawn into the pitch cooler, a closed tank with a manhole having a loose-fitting, free-opening lid which, while it acts as a safety valve, prevents free access of air. The pitch, when sufficiently cooled, is filled directly into barrels for shipment or storage.

The fraction to 200° C. contains water, ammoniacal liquor, crude benzols, pyridine bases and a part of the naphthalene, heavy oil and phenols. The second fraction from 200° C. to soft pitch (about 270° C.) consists of phenols, naphthalene, heavy oil and some anthracene, though the greater part of the anthracene comes over above 270° C. If the distillation is continued to hard pitch, a cut could profitably be made at about 270° C., above which point most of the anthracene and anthracene oil would be obtained. The treatment of the fractions as obtained by American practice only will be considered, with incidental allusions to the foreign methods.

Treatment of Light Oil—The light oil fraction is allowed to settle and the ammoniacal liquor or water is drawn off. The pyridine[2] bases are not as a rule recovered in this country, but are allowed to remain in the heavy oil with the phenols. If it is desired to separate them, the light oil is agitated with dilute sulfuric acid in a lead-lined cone-bottomed tank, fitted with a lead-covered propeller, usually supported entirely outside the tank, which mixes the contents. After the pyridine bases have been removed the oil is transferred to a similar iron tank, in which, in order to remove the phenols, it is treated with caustic soda solution of about 1.116 specific gravity, converting the phenol to sodium phenolate. After the phenolates have been drawn off, the oil is charged in a still of 2000 to 3000 gallons capacity, similar to a tar still, but having in addition a column and condenser for the rectification of the vapors coming from the still. (See Figures 3 and 4.) It is operated as a batch still and the following fractions are usually taken:

Crude 90 per cent benzol, to 95° C.
Crude toluol, 95° to 125° C.
Crude solvent naphtha, 125° to 170° C.
Heavy naphtha, 170° to 200° C.
Residue.

The residue consists of naphthalene, heavy oil, and phenols if not previously extracted. It should be added to the second fraction from the tar still.

In some works only three fractions are made in the light-oil still, the first two being combined and this fraction being subjected, before washing, to another

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[2] See Compound 476, Chapter 27.

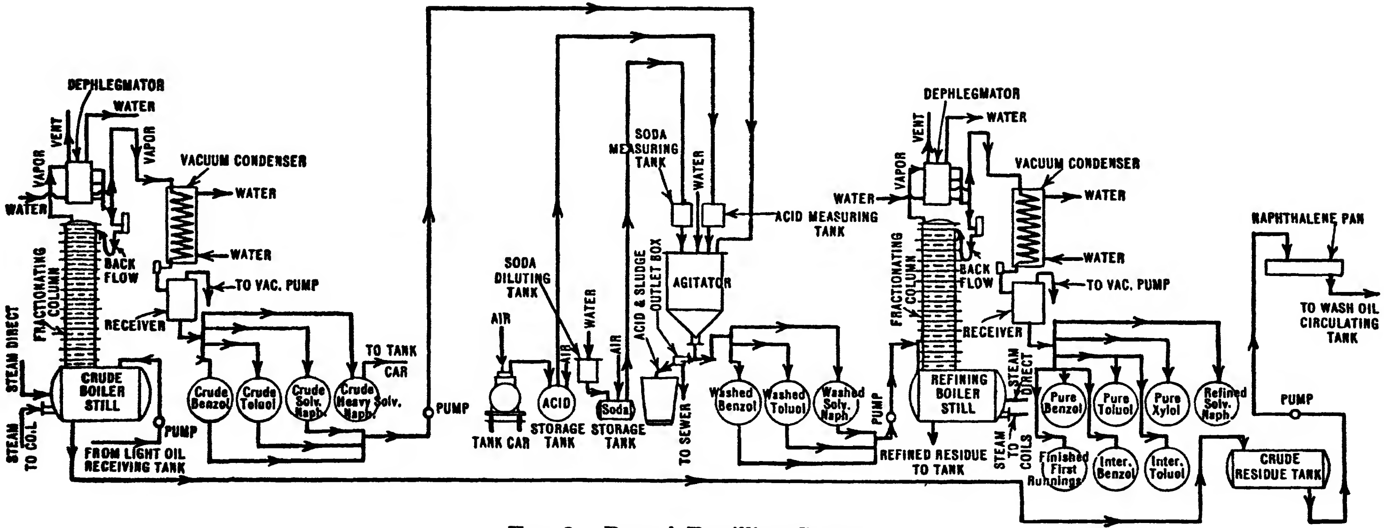

FIG. 3. Benzol Distilling System.

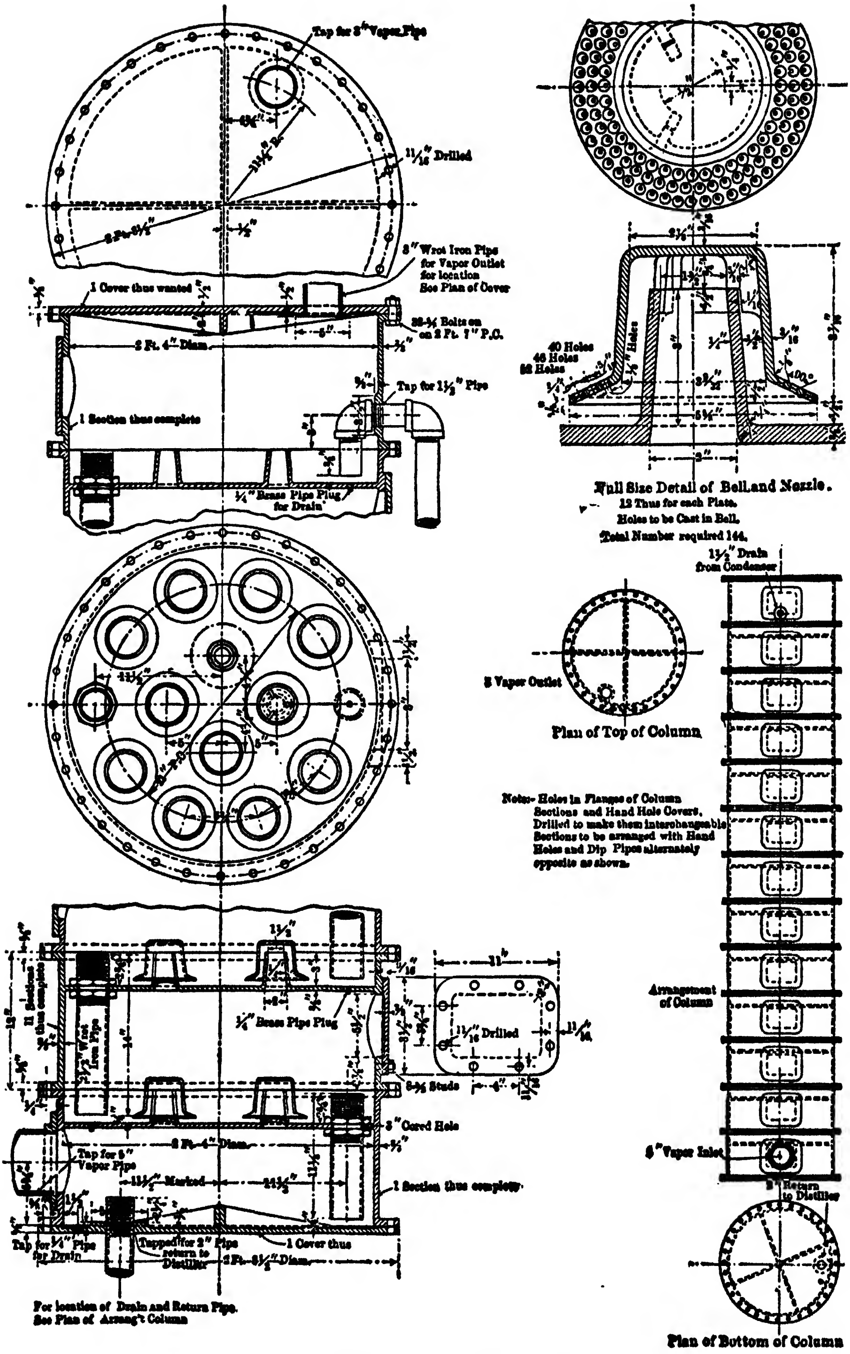

FIG. 4. Detail of Distilling Column.

distillation in a steam-heated column still. The fraction, consisting of benzene, toluene, xylene, and their impurities, would be cut as follows:

Crude 90 per cent benzene	up to 99° C.
Intermediate fraction (which is rerun)	95° to 105° C.
Crude toluene	105° to 120° C.
Crude solvent naphtha added to that fraction	120° to 125° C.

It was early discovered at the Paris Gas Company that the coal gas contained much more aromatic hydrocarbons than the tar. It was variously estimated at from 15 to 23 times as much but the gas was not seriously considered as a source of benzol while only illuminating gas was manufactured from coal.

LIGHT OIL RECOVERY FROM GAS[3]

When by-product coke ovens became common in Europe, processes were devised to scrub the gas and recover the light oil by continuous distillation. Figure 5 is a diagram of the usual apparatus employed.

The gas is cooled either by direct contact with water or in tubular coolers to about 70° F. or even less. It is then passed through the series of scrubbers (usually three), where it comes in intimate contact with the cooled wash oil which is about the temperature of the gas entering the system, but should not be more than 2° to 4° F. higher.

The scrubbers may be of almost any design suitable for washing gas. The usual form is shown in Figure 5. These are tall steel tanks or towers filled with wooden grids to present large surfaces for the contact of the oil and gas.

The wash oil used in the United States is a fluid paraffin oil, specific gravity not more than 0.875 at 18° C., not thickening above 4° C., containing as little olefins as possible, not more than 10 per cent. Not more than 1 per cent shall be driven over by steam distillation while collecting a volume of condensed steam equal to the volume of the oil taken for the test, and it should separate readily from intimate mixtures with water. The average molecular weight of the wash oil is usually about 240.

After leaving the first gas scrubber the oil is passed through a heat exchanger, where it is heated by the vapors leaving the still to about 90° C., then through a second heat exchanger, where it is further heated by the debenzolized wash oil, leaving the still at about 110° C.

It is then passed through the preheater and further heated by steam to 130° to 150° C. After this it passes to the still proper, which is of the continuous type, where the light oil is driven out by steam distillation, leaving the debenzolized oil, which leaves the base of the still, passes through the oil to oil heat exchanger, the wash oil coolers, and is then ready to be pumped to the scrubbers for resaturation with light oil from the gas. The light oil vapor mixed with steam after passing through the vapor to oil heat exchanger is condensed and flows to the light oil tank after being separated from the condensed steam or water in the decanter.

The yield of light oil from coke oven gas is from 2¼ to 4 gallons per ton of dry

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[3] See also Chapter 15.

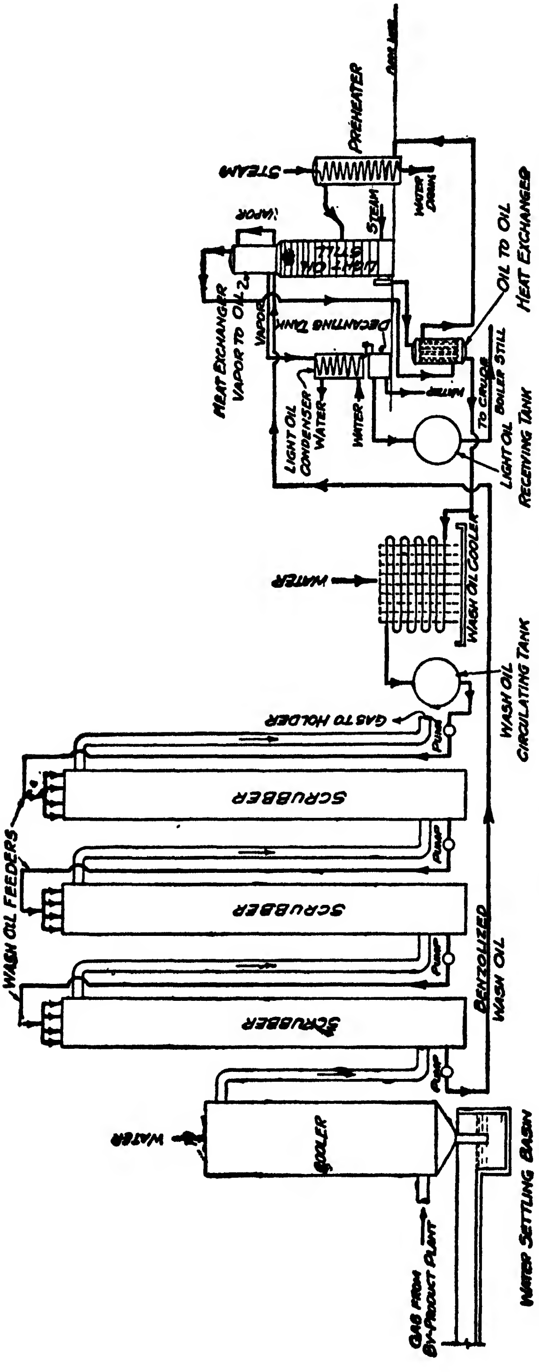

FIG. 5. Diagram of Apparatus to Recover Light Oil from Gas.

coal carbonized, varying with the volatile content of the coal and much influenced by the type of oven and the heats employed. The relation of the amounts of benzol and toluol produced are also influenced by the heats employed, low heats increasing the production of toluol and xylol. The recovery of light oil from coke oven gas has become general in American by-product coking practice.

The principal constituents of the light oil vapors are benzol (B.P. 79.6° C.), toluol (B.P. 110.8° C.) and xylenes (B.P.'s 138.5, 138.8 and 144° C.). Only a small amount of the wash oil is carried over in the vapors, but the small amount of high boiling fraction contains a large number of heavy compounds.

Purification of Light Oil—Light oil is usually fractioned in a steam-heated column in order to yield crude benzol distilling 90 per cent to 100° C., crude toluol distilling about 5 per cent to 100° C. and 90 per cent to 120° C., crude solvent naphtha containing the xylenes distilling about 5 per cent to 130° C. and 90 per cent to 160° C., crude heavy solvent naphtha distilling about 5 per cent to 160° C. and 90 per cent to 200° C. The residue consists of wash oil and crude naphthalene. It is transferred to pans and allowed to become cold, when the naphthalene crystallizes. The wash oil is drained off and returned to the wash oil circulating tank to be used over again.

The crude fractions are washed and refined in the same manner as similar fractions of the light oil from tar.

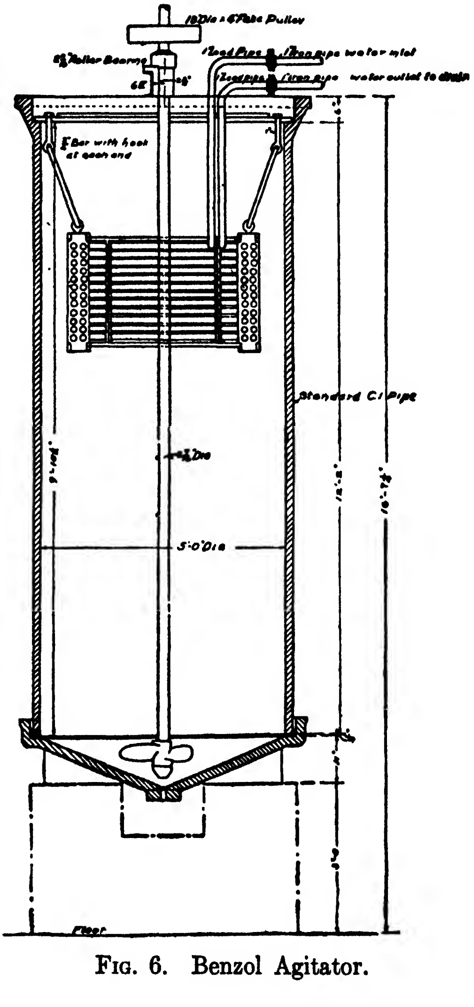

FIG. 6. Benzol Agitator.

The purification of these fractions consists in the polymerization of the unsaturated compounds and the removal of the dissolved polymerized hydrocarbons by distillation. The oil is first treated with successive small portions of sulfuric acid, 1.835 sp. gr., in an agitator tank (Figure 6) similar to the one used for pyridine extraction. The agitator for washing with strong acid can be lined with lead. A better construction is of cast iron with leaded joints of the bell-and-spigot type, similar to those used on water pipes, with a conical bottom to permit of complete separation of the acid and the oil. Since the advent of electric welding agitators can be made of steel with all joints welded.

The several small portions of acid are agitated with the oil, allowed to settle for a few minutes and then the acid tar composed of spent acid and polymerized hydrocarbons is drawn off. Care must be taken to remove the tar completely after the final application of acid. The acid necessary for a satisfactory purification of the oil should be determined by a laboratory test after each addition of acid. If too little acid is used, the tarry products are apt to separate and clog the drawoff, and if too much is used the spent acid will be very thin and fluid. A good wash is usually obtained when a total of between ⅓ and ¾ of a pound of acid is used per U. S. gallon and applied in four to six successive portions. In this way a better wash and a larger yield will result, together with a saving of acid. The oil is finally treated with sufficient 10 per cent caustic soda solution to remove all traces of acid. The washed oil is sometimes distilled in a steam-heated simple still, but this is not necessary with the fractions of light oil recovered from coal gas, which leave behind, as a viscous mass, the polymerization products that were dissolved in the oil. This residue is reported to have some application in waterproofing paper.

The final fractioning of the refined oils is conducted in steam-heated bubble cap column of 20 to 30 plates. (See Figure 3.)

Benzol—The crude benzols from light oil are colorless when freshly distilled, but they soon become a pale straw color and continue to darken for some time. They are known in the trade as crude or "straw-color" benzols of the various grades.

TABLE 6—CRUDE BENZOL GRADES

Fraction	*Specific Gravity*	*5-10 Per Cent*	*90 Per Cent*	*Dry*	*Flash-point*
Straw-color benzol	0.860-0.885	80° C.	100° C.	120° C.	below 0° C.
Crude 90 per cent benzol					
Straw-color toluol	0.860-0.875	100° C.	120° C.	140° C.	below 0° C.
Crude toluol					
Crude solvent naphtha	0.870-0.885	130° C.	160° C.	190° C.	22-26° C.
Heavy naphtha	0.925-0.940	160° C.	210° C.	220° C.	43-45° C.

These crude oils are chiefly used as solvents where their odors are not objectionable. Crude solvent naphtha and heavy naphtha are also used as thinners in certain cheap paints. Benzol is also used as motor fuel and in numerous chemical syntheses.

Of the refined oils three are separated in a pure state, C.P. benzol, C.P. toluol, and xylol. The first two distill entirely within 2° C., while the last is a mixture of the three xylenes and distills from 135 to 145° C.

C.P. benzol or benzene has sp. gr. 0.875 to 0.884. Freezing point 4° C., boiling point 79.6° C. It should distill completely within 2° C., be colorless and have the characteristic odor. It should not be colored on shaking with one-third its volume of C.P. sulfuric acid, 1.84 sp. gr. (96 per cent H_2SO_4), and the acid should be only slightly colored after standing for one-quarter of an hour. It should be free from thiophens, contain only traces of carbon disulfide and from 1 to 3 per cent of inert paraffins.

Toluol—C.P. toluol or toluene has sp. gr. 0.865 to 0.876, boiling point 110.8° C. It should be colorless and have the characteristic aromatic odor. It should not be colored by shaking with one-third its volume of C.P. sulfuric acid, sp. gr.

1.84, and the acid layer should not be colored deeper than a pale straw after standing for one-quarter hour. In other respects it should answer the specifications for C.P. benzol.

The constants of the refined commercial fractions are given in Table 7.

TABLE 7—GRADES OF REFINED BENZOLS AND NAPHTHAS

Fractions	*Specific Gravity*	*Temperatures Noted in Distillation*			*Flash-point*
		80° C.-90° C.	100° C.	120° C.	
100% benzol	0.875-0.885	5-10%-90-95%	dry		below 0° C.
90% benzol	0.865-0.880	0%	90-92%	dry	below 0° C.
		100° C.	120° C.	135° C.	
50% benzol	0.862-0.880	50-52%	90-92%	dry	below 0° C.
Commercial toluol	0.865-0.875	0-5%	90-95%	dry	below 0° C.
Solvent or 160°		130° C.	160° C.	185° C.	
naphtha	0.860-0.870	0-5%	90-92%	dry	22-26° C.
		160° C.	200° C.	215° C.	
200° naphtha	0.879-0.882	0-10%	90-92%	dry	42-45° C.

Creosote or Heavy Oil—The fraction from the tar still between 200 and 270° C., and sometimes even higher, contains most of the phenols, naphthalene, anthracene, and the accompanying oils. Anthracene will be found in large quantities only when the distillation of the tar is carried to hard pitch.

If it is desired to remove the tar acids (phenols) the oil is agitated at a temperature of 50 to 70° C. with sufficient caustic soda solution, sp. gr. 1.116, to combine with them. The alkaline liquor is allowed to settle and is drawn off, after which the oil is run into shallow tanks or pans, where a large part of the naphthalene separates out as a mass of crystals when the oil cools. It is possible to treat the oil with successive portions of the caustic soda solution to obtain, first an alkaline solution in which sodium phenolate preponderates; second an equally pure sodium cresylate; and third an unsaturated solution of caustic soda and sodium cresylate which is used as the first portion on the succeeding charge.

The portion containing principally sodium phenolate is boiled by direct steam, and air is passed through the boiling liquid to remove naphthalene, hydrocarbon oils, and pyridine bases. In some works the distillate from the boiling carbolate is collected and worked for pyridine and naphtha, in which case the boiling is done by fire-heated still instead of by direct steam.

The distillate is collected until the purification is nearly complete, when the manhole is opened and direct steam and air blown through the liquor. After this treatment the sodium phenolate should be soluble in water without turbidity. The purified phenolate solution is allowed to become cold and is saturated with carbon dioxide, usually obtained from the flue gases from the steam boilers. Finally, after the sodium carbonate solution formed has been drawn off, the decomposition is completed, in a lead-lined tank, by a little dilute sulfuric acid, which also aids the separation of the phenol from the aqueous solution. The sodium sulfate solution is carefully and completely drawn off. The crude phenol thus obtained contains from 20 to 25 per cent water and tar. These are removed by distillation in a still similar to a tar still, although much smaller. The dry, crude phenol is fractionated in column stills heated by direct fire or superheated steam, but otherwise the stills are similar to those used for benzols. These yield, first, a crystallizable phenol, second, a fraction not sufficiently rich in phenol to crystallize, and a third fraction containing principally cresols. (Vacuum distillation is used at some works to separate phenol from its crude.) By this process, owing to the low temperature of the distillation, a larger yield of phenol is obtained.

The crystallizable fraction is further purified by repeated crystallization with the aid of refrigeration and with the addition of water in the last crystallization, to dilute the cresols present. Finally, these purified crystals are redistilled, condensed in block-tin worms and collected in tin receivers so arranged that they can be heated to melt the phenol in order that it may run in a liquid state into containers.

The second portion of the alkaline liquor from the treatment containing largely sodium cresylate is saturated with carbon dioxide and sulfuric acid in the same manner as is the portion rich in phenol. It is not customary to boil the sodium cresylate to remove the oils and pyridine bases unless it is desired to make pure cresol. The crude cresol is freed from tar and water by distillation and is then marketable as 95 to 100 per cent cresylic acid.

PROPERTIES OF THE PRODUCTS FROM THE LIGHT OIL FRACTION

Phenol,[4] C_6H_5OH, when pure, is a white, crystalline mass, with sp. gr. 1.084 at 0° C., melting at 42° C., boiling at 182° C., having a characteristic odor and, when very dilute, a sweetish taste.

It is soluble in all portions in alcohol, ether, chloroform, glacial acetic acid, and glycerine. It liquefies on the addition of 14 to 15 per cent of water, and thus becomes the No. 4 carbolic acid of commerce. It dissolves in about 20 parts of water at 25° C. It is a corrosive and irritant poison. Undiluted alcohol is one of the best washes for phenol burns. Carbolic acid is largely used in medicine and surgery as an antiseptic and disinfectant and in the arts in the manufacture of dyes.[5] It is employed in the manufacture of picric acid, trinitrophenol,[6] which finds a large use in the manufacture of high explosives and is also used as a yellow dye.

Cresol,[7] cresylic acid, hydroxytoluene, $C_6H_4CH_3OH$, is a mixture of three isomers, has a sp. gr. of 1.032 to 1.038 at 25° C., and distills between 190° and 205° C. It is used as an antiseptic and disinfectant and is much less corrosive than phenol and is a more efficient antiseptic.

The three isomers composing cresol have the following properties:

Orthocresol, orthocresylic acid, ortho-oxy-toluene, orthomethylphenol, $C_6H_2OH(CH_3)$, with the CH_3 and OH groups in the $(1-2)$ position, is a white crystalline substance melting at 28 to 30° C. into a colorless liquid and boiling at 187 to 189° C. It is soluble in thirty parts of water, in alcohol, ether, chloroform, and the caustic alkalies.

Metacresol, metacresylic acid, meta-oxy-toluene, metamethylphenol, has the CH_3 and OH groups placed in the $(1-3)$ position, and is a colorless liquid, sp. gr. 1.0498 to 1.05 at 0° C. It boils at 202° C., is soluble in alcohol, ether, chloroform, caustic alkalies, and slightly in water.

[4] See Compound 291, Chapter 27.

[5] See Chapter 28.

[6] See Chapter 32.

[7] See Compound 208, Chapter 27.

Paracresol, paracresylic acid, para-oxy-toluene, paramethylphenol, with the CH_3 and OH groups placed in the (1—4) position, is a white crystalline mass, melting at 36° C., and boiling at 198° C. It is soluble in alcohol, ether, chloroform, caustic alkalies, and slightly in water.

Xylenol,[8] di-methyl-phenol, hydroxy-xylene. The six possible isomers are probably present in the fraction of crude cresylic acid boiling between 210° and 230° C. and which has a sp. gr. between 1.02 and 1.03 at 15° C. They are on the whole considerably more soluble in water and less corrosive than the cresols. They are used in disinfectants of the "creolin" type, as a solvent, and in organic synthesis, particularly of dyes. They are not generally separated from the crysilic acid except when pure cresols are made.

OTHER TAR PRODUCTS

Recovery of Naphthalene—The heavy oil fraction, if the removal of the naphthalene is desired, is run into shallow tanks or pans, either from the still or after the tar acids have been extracted, and allowed to become cold, when the larger part of the naphthalene crystallizes. The oil is drawn off and the crystals are either shoveled into piles to drain or are passed through a centrifugal which leaves the crystals nearly dry and in condition for market as "drained creosote salts" or crude naphthalene.

Refining naphthalene consists in freeing it from adhering heavy oil and from unsaturated, easily oxidized compounds. The crude material should be in a coarse crystalline condition to allow of the proper extraction of the oil. If it is in a slimy state it should be recrystallized. The crystals are either washed with hot water in centrifugals, which removes the larger part of the adhering oil, or they are hot pressed in hydraulic presses. The latter process is more expensive and less efficient than the former. After this operation the naphthalene should have a melting point of not less than 76° C., and will still contain from 4 to 6 per cent of oils. The partly purified naphthalene is now distilled, to remove the tarry bodies that have been carried forward from the original tar. This process is conducted in plain, externally fired iron stills, similar to tar stills, but with lead worm condensers. The distillate is kept in a melted state and run into lead-lined agitators similar to those used for benzols, and washed with sulfuric acid, 1.835 sp. gr., several waters, and finally with caustic soda solution, of about 1.116 sp. gr. Great care must be taken to remove as much as possible of the acid before the first water is added so as to prevent the tarry polymerization products from being redissolved by the naphthalene. The soda solution is drawn off completely, as small amounts of soda will cause the bottom of the still to be rapidly burned out. It is necessary to reject the first portion "heads," and the last portion, "tails," of the distillate from the final distillation of refined naphthalene, as the "heads" are discolored by the washings of the condenser and with water containing dissolved bases, metallic salts, etc., while the oils are concentrated in the "tails." The sum of the rejected portions should not exceed ½ to 1 per cent of the distillate.

The water-white refined naphthalene is run into shallow pans to cool, when it

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[8] See Compound 334, Chapter 27.

can be broken up and sold as lump, or is run into copper tanks heated by steam, from which it is available for casting into balls, etc., or for use in the subliming pans. Subliming pans, Figure 7, are large shallow iron tanks heated by steam and connected by an iron hood with a smoothly sheathed room in which the sublimed vapors condense in transparent plates, "flake naphthalene." About 150° C. seems to be the most satisfactory temperature in the subliming pans. A higher temperature can be economically employed in winter and a somewhat lower one in summer.

Naphthalene,[9] $C_{12}H_8$, is a solid hydrocarbon at ordinary temperatures, melting at 79-80° C., and boiling at 218° C. Its specific gravity in the solid state is 1.151 at 15° C. and in the liquid state it is 0.9778 at 80° C. It volatilizes at ordinary temperatures and very readily on the steam bath. It crystallizes in transparent rhombic plates, which are slightly soluble in hot water but insoluble in cold water. It is very soluble in chloroform, benzene, ether, alcohol, methyl alcohol and paraffin.

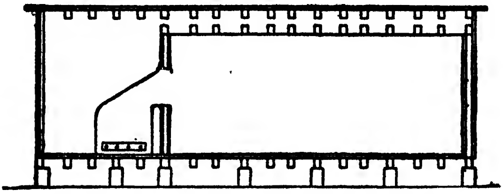

Fig. 7. Naphthalene Subliming Plant.

Naphthalene is used as the starting-point of several classes of colors, including nearly all of the azo-colors and for artificial indigo, in candles, celluloid, as a substitute for camphor to prevent moths in woolens, in the manufacture of phthalic anhydride for plastics, and to some small extent as a gas enricher in lights of the albo-carbon type. It readily nitrates directly to mono-nitro naphthalene, which crystallizes in yellow needles, with sp. gr. 1.331 at 4° C., melting at 56° C., and boiling at 304° C. It is easily soluble in alcohol and petroleum oils. Its principal uses are the manufacture of dyes and to remove the fluorescence from petroleum oils, for which latter purpose from 2 to 3 per cent is used.

Anthracene Oil—This oil is the portion of the distillate from coal tar which vaporizes above 270° C. At this temperature a cut should be made if the distillation is carried to hard pitch. This oil boils between 250 and 400° C., and has a specific gravity of nearly 1.1. Its color is yellowish-green when first made, but it darkens to almost black. Besides anthracene, it contains naphthalene, methylnaphthalene, pyrene, acridene, phenanthracene, fluorene, etc., all of which are solids, except methylnaphthalene, and a mixture of oil of which we know very little.

The anthracene fraction is run into shallow tanks and the solid compounds separate out on cooling. This process requires from one to two weeks.

Refrigeration has been tried to shorten the time, but it makes the oils more viscous and the separated crude anthracene much more impure. The semi-solid mass is transferred to bag filters or to a filter press and as much as possible of

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[9] See Compound 360, Chapter 27.

the oil driven out by compressed air. The nearly dry cakes from the bags or filter press, containing about 10 to 15 per cent anthracene, are subjected to a pressure of from 50,000 to 70,000 lbs. in hydraulic presses so arranged that they may be kept hot by steam coils or steam-heated plates. This treatment brings the anthracene content to 25 to 35 per cent. These press-cakes are ground and purified by washing in a closed agitator with hot solvent naphtha from the light oil.

Lower boiling benzols have been used for this purpose, but they dissolve the anthracene itself. The whole charge, when thoroughly mixed, which may require several hours, is run into a closed filter and the solvent removed by compressed air. Pyridine bases are said to be a better solvent for the anthracene impurities than solvent naphtha and are said to yield 80 per cent anthracene, while 70 to 75 per cent is the limit with solvent naphtha.

A somewhat purer anthracene is produced by the sublimation of the washed material. The subliming pans are similar to those used for naphthalene except that they are heated by fire and have jets of superheated steam impinging upon the surface of the melted anthracene. The vapors are condensed by water jets. The oil from the crystallization of the crude anthracene is distilled in a clean still until crystals appear upon cooling the distillate, when the residue containing the anthracene is run into pans and treated the same as the original fraction.

When the oil will yield no more anthracene it is used to soften, "cut back," pitch, as "Carbolineum Avenarius," for the treatment of timber, or mixed with the creosote oil.

Anthracene,[10] $C_{14}H_{10}$, was discovered by Dumas and Laurent in 1832 and recognized as a characteristic constituent of coal tar by Fritzsche in 1867. It boils at 363° C., melts at 213° C., and has a specific gravity of 1.147 at 15° C. It crystallizes, when pure, in white or yellow rhombic plates with a blue fluorescence. It is soluble in benzene, ether, chloroform, carbon bisulfide, and in hot alcohol, but only sparingly soluble in cold alcohol.

It is slowly converted by sunlight into paranthracene. It is of great importance commercially as the starting-point for the synthetic alizarines.[11]

FUTURE OF COAL TAR PRODUCTS

The items which have just been discussed cover only a few of the more important materials which can be recovered from coal tar. Like petroleum, coal tar can serve as a source of an almost limitless number of organic compounds. In the case of tar, the compounds are for the most part the aromatics while petroleum is commonly a source of aliphatics. The future of the coal tar industry is undoubtedly tied up with the extent to which its products can be used as chemical raw materials for further syntheses.

When synthetic dyes first came into manufacture, it was a great boon to the coal tar industry, but as the production of by-product tar increased the chemical demand never kept up with the supply so that coal tar is now a very inexpensive commodity and the chemical uses by no means take care of all of it. If, as is happening in petroleum, new uses and outlets in the making of a

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[10] See Compound 431, Chapter 27.
[11] See Chapter 28.

large number of new compounds, such as plastics, can be found for coal tar, then it is quite likely that it will become an increasingly important source of raw material for the chemical industry. It is by no means certain but it is quite possible that this will be the trend that it will take.

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CHAPTER 17

WOOD DISTILLATION INDUSTRY

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In the hardwood distillation industry, hardwood is heated to produce such products as charcoal, wood alcohol and acetic acid.

Whenever a complicated organic material such as wood is heated out of the presence of oxygen, thermal decomposition (pyrolysis) occurs and a great many new products are formed which often bear but little chemical resemblance to the parent material. In general, however, it may be said that the products of the thermal decomposition of wood are compounds of lower molecular weight than the original material. Moreover, the compounds which are of sufficiently low molecular weight to be vaporized at the o[illegible]mperature contain a much smaller proportion of carbon, by w[illegible]an the original wood. Hence, carbon atoms are left behind in the for[illegible]f charcoal. The destructive distillation[1] of wood, then, yields four types [illegible] products: (1) non-condensable gases, usually inflammable, (2) condensable vapors which are given the catch-all name of pyroligneous acid, (3) charcoal, and (4) tar.

In the early days of wood distillation, charcoal was the only product and no attempt was made to recover the volatile materials. But while chemical industry was still a mere struggling infant, the recovery and refining of the pyroligneous acid and tar became an important item. The by-product liquid of hardwood distillation now yields principally wood alcohol (methanol), acetic acid and acetone. A multitude of other materials is present in pyroligneous acid and tar, but only in small proportion. Their recovery is of only minor importance.

THE ECONOMIC PICTURE BEHIND THE WOOD DISTILLATION INDUSTRY

Wood distillation plants were originally built to supply a large charcoal market. However, with the advent of coke for use in blast furnaces and the development of superior domestic heating methods, the industry found that the charcoal market was rapidly shrinking. Dwindling business meant dwindling profits and it became necessary to make a more complete recovery of wood distillation products. Aside from charcoal, methanol, methylacetone, acetate of lime, and tar were recovered by the hardwood distillers. This recovery of by-products revived the industry to a very large extent.

Beginning with the 1920's the industry was beset with another difficulty—the competition of synthetic chemicals. Chemical competition developed rapidly

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[1] For a discussion of the general principles of thermal decomposition see Chapter 3, The Unit Processes.

to the point where the synthetic chemical industries were able to compete, particularly in the production of methanol and acetic acid, and finally to the point of controlling the market for these products.

Confronted by a shrinking charcoal market and unable to overcome the competition of synthetic chemicals, the hardwood distillation industry, except for a few fluctuations in the early 1900's, has steadily declined. Table 1 illustrates this decline in the hardwood field and the trend is the same for the wood distillation industry in general. Charcoal remains the essence of the industry. So long as the distillers can sell their charcoal the industry is able to operate successfully. The demand for charcoal has apparently become fairly well stabilized, although it is now greatly reduced compared to original consumption. Figures for the year 1935 indicate that the decline has leveled out at a point where the value of the products of the hardwood distillation industry approximates $7,500,000 yearly.

TABLE 1—SALIENT STATISTICS OF THE HARDWOOD DISTILLATION INDUSTRY OF THE U. S.*

Year	*Establishments Active*	*Wage Earners*	*Wood Used (Cords)*	*Value of Products Sold*
1909	116	2200	1,150,000	$ 9,500,000
1914	82	2300	970,000	9,400,000
1919	87	3500	1,186,000	27,000,000
1921	72	1521	433,000	8,278,000
1923	76	2923	1,030,000	24,262,000
1925	67	2866	911,000	16,871,000
1927	57	2898	822,000	17,414,000
1929	53	2838	812,000	19,478,000
1931	42	1800	440,000	7,400,000
1935	60	3808	......	7,700,000

* Data from McBride, R. S., Chem. & Met. Eng. *39*, 534 (1932), and "Commodity Markets in Chemical Consuming Industries," ibid. *44*, 579 (1937).

More complete recovery of distillation products by fractionation of the tars and recovery of turpentine, pine oil, rosin, and other wood products from softwood distillation has greatly aided the industry. For example in the year 1935 the value of hardwood distillation products was about $7,500,000, but the value of the turpentine, pine oil, and rosin recovered from pine wood raised the total to almost $16,000,000. That there is at least a minor upswing in the industry over the low points of 1931 is indicated by the fact that by 1935 there were 60 wood distillation plants in the country demanding the services of some 3800 workers. Continual activity towards complete product recovery plus a certain permanent demand for charcoal seems to be the formula for future successful operations in the industry.

This story of the economic difficulties of the wood distillation industry is a good example of the competition between natural and synthetic products discussed in Chapter 1, The Economic Pattern.

HARDWOOD DISTILLATION

The location of plants using hardwood for destructive distillation is dependent upon a number of factors such as nearness to the supply of wood, the cheapness of the raw material and the ultimate use of the products which are to be made.

At the present time, plants are located in Northern New York and Pennsylvania, Michigan and Wisconsin and in Tennessee and Arkansas where hardwood abounds. Because of severe competition from other processes, the expansion of the hardwood industry is not likely. Within the last ten years over one-half of the then existing plants have closed down permanently. Of the remaining plants, the prospects are that they will be able to maintain themselves because of local conditions which are favorable for more successful operation.

There seems to be sufficient raw material to supply all existing plants for a long period of time. Where the supply of wood seems to be scarce, conservation methods are being employed which will tend to increase the life of the plants. The actual amount of wood distilled per year is not great, relative to annual growth of the forests.

Considerable quantities of wood are brought in by farmers and truckers during their idle time. The cost of such wood is approximately five dollars per cord delivered, for sticks 48″ to 52″ in length. The diameter is 4″ maximum, although at one plant a 5′ stick is allowed and a diameter of 6″ maximum.

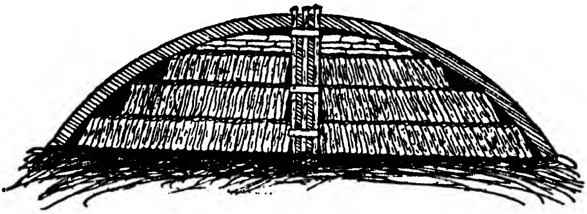

Fig. 1. Charcoal Pit.

If continuous processes are to be employed, it is necessary to chip the wood. Sawmill waste is usually cut up into blocks, no sawdust or bark being used.

Equipment—*Charcoal Pits.* In the early days, when charcoal alone was to be made, pits (Figure 1) and kilns were used. These were fired from the bottom, and just enough air admitted to burn enough wood to furnish the heat to distill the remainder. The air originally in the kiln had to be forced out at a low temperature in order to avoid explosions. Such equipment is now obsolete as far as the general industrial picture is concerned.

Cylindrical Retorts. The simplest form of apparatus for carrying out the operation when distillation products are to be recovered consists of an enclosed vessel, called a retort, which is surrounded by a suitable furnace. The retort is supplied with a vapor line which connects with a condenser. The condensed product is then collected in a suitable storage tank. Since acid is liberated by the distillation, it is necessary to use acid-resistant materials of construction. Steel retorts, a copper condenser and vapor lines, and copper-lined or wooden receiving tanks are commonly employed.

At first, batteries of small retorts were used. These were about 9 ft. long by 50″ in diameter and held nearly a cord of wood each. They were connected with a condenser for cooling the vapors. They were charged and emptied by hand. An iron box mounted on wheels was used to hold the hot charcoal, and when it was full, it was covered with a sheet iron cover and the edges luted with sand or clay. Some of these retorts are still in use. See Figure 2.

Oven Retorts. The oven type of retort is shown in Figures 3 and 4. These are the most universally used. They are rectangular in shape, flat on the bottom and slightly arched on the top. They are about 6 ft. wide and 7 to 8 ft. high and of various lengths to hold two, three or four cars each. The bottom is supplied with rails upon which the cars of wood are rolled. In the sides or back are one or more openings for the exit of the vapors to be condensed. The wood is loaded on steel cars holding about 2 to 2½ cords each and rolled into the retort. They are also supplied with a storm door in front and a hood and stack to take vapors away when the doors are opened for withdrawing the hot charcoal.

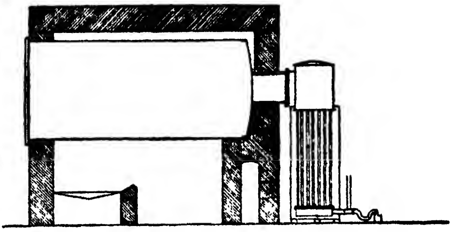

FIG. 2. Cylindrical Retort and Condenser.

Two coolers are used with each of these ovens, of similar shape to the ovens but made of lighter material, into which the car of charcoal is drawn soon after the end of the distillation. A European suggestion added a preheating and drying zone to the ovens to dry the wood before actual distillation takes place. A modification of this idea is now in use. It is of particular advantage in distilling green wood as it saves weather drying of the wood.

Retorts for Chipped Wood. For using chipped wood a number of types of retorts have been tried. One of these, the Seaman retort, is a rotating cylinder 36 ft. long and 3 ft. in diameter, sloping downward toward the discharge end at the rate of ½″ per foot in length. A plunger type of feed is at the upper end and as the retort rotates the material works its way to the lower end and is discharged as finished charcoal. It is possible that new developments may make this operation satisfactory, but so far after repeated trials, it has not been so.[1a]

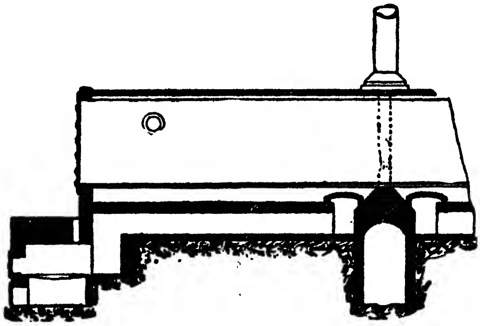

FIG. 3. Steel Oven Retort.

Condensers. The most satisfactory condenser seems to be the vertical tubular condenser which is shown in Figure 2. It consists of a vapor pipe leading to an expanded chamber at the top followed by the necessary condenser tubes and a bottom chamber for collecting the liquid formed on the tubes—these parts all made of copper. The whole is contained in a steel shell through which the condensing water flows. The condenser is furnished with a cap or removable top fastened by means of a yoke or bolts so that the tubes can be easily reached and cleaned. To the lower chamber is connected an outlet pipe which is usually

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[1a] Haertel, M. H., "Timber Requirements of the Hardwood Distillation Industry," p. 45, Forest Service Bulletin (1938).

supplied with a "goose-neck" or U-bend, to hold back the gases, and a top opening in the bend to permit the gases to escape through a pipe leading to the boiler furnace. The bottom of the condenser is made sloping so as to allow the tar to drain out.

Worm condensers could be used and also tubes set one above another, with removable ends, but the tubular condensers are more easily cleaned.

Operating Methods—Carbonization—To carry out the operation of destructive distillation, no definite rule can be followed. Some operators find that the temperature required varies with the different woods and the time of distillation varies with the temperature. Some woods distill rather easily and others with difficulty. The yield of condensed products varies greatly with the firing. The charcoal made at a given temperature also varies in composition according to the kind of wood used. The proper conditions should always be determined by experiment when a new variety of wood is used.

FIG. 4. Oven Retort. (Courtesy Dr. D. F. Othmer, Brooklyn Polytechnic Inst., Brooklyn, N. Y.)

Showing double doors, rails, condenser outlet and interior of the oven.

To operate to the best advantage, the air in the retort must be removed before too great heat is applied, as otherwise an explosion may take place. After the air is expelled, rather rapid heating can take place, in order to start the flow of liquids from the condenser. As overheating causes a loss of volatile liquids, it is better to slow down the heating after this point. There is also a tendency for pressure and temperature to increase suddenly due to exothermic reactions. After reaching a certain temperature, which can be ascertained by suitable pyrometers, the heating can be increased quite rapidly in order to drive out the heavy tars.

The first distillate begins to come over at about 320 deg. F. (pyrometer in retort and not in vapor line) and consists of furfural, water and a very little acid. The watery distillate is known as pyroligneous acid. The percentage of acid increases with the increase in temperature and quantity of distillate, until the tar begins to distill, then it begins to drop off slightly. Meanwhile, non-condensable gases are formed and these are piped to the furnace and burned. Sometimes these gases are scrubbed with water before being burned. During the earlier stages of the distillation, the color of the burning gas is blue, due to the carbon monoxide present, while later on the color becomes yellow due to the presence of the heavier hydrocarbons. The end of the distillation is indicated by the falling off of the quantity of distillate, by the temperature inside of the retort (about 700 to 800 deg. F.), and by the color of the shell of the retort. The character of the distillate also indicates the end of the distillation, the tarry products being strongly in evidence. When cars are used, the charcoal is withdrawn very quickly, thus saving the heat of the brickwork for the next charge. The conditions should be regulated so that each retort can be charged once every twenty-four hours, allowing two hours for cooling before withdrawing the charcoal. The fuel used for firing the retorts is usually oil, natural gas or coal. It requires about ¾ of a ton of coal or its equivalent to distill a cord of wood.

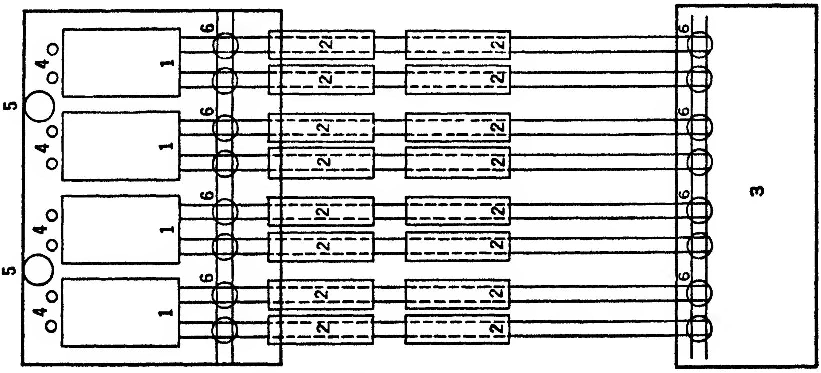

Fig. 5. Ground Plan of Oven.

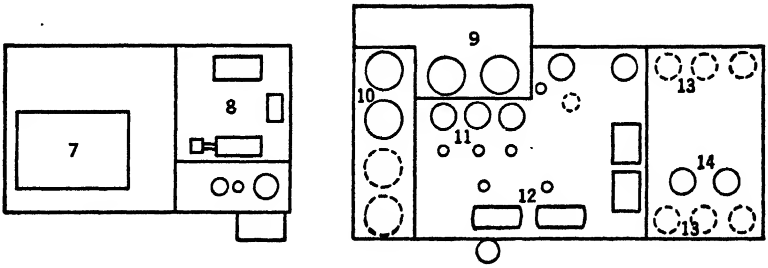

Fig. 6. Ground Plan of Refinery.

The ground plans of an American hardwood distilling plant are shown in Figures 5 and 6. Furnaces with two ovens each are shown at 1, 1, 1, 1. The wood is brought to the turntables 6, in special cars. These cars are pushed into the ovens and the doors of the ovens closed. The doors are tightened by driving wedges around the edges. The vapors from the distilling wood are condensed in tubular condensers 4, and the condensed liquors collected in tanks 5. The cars of charcoal are pulled while hot and taken to a series of coolers 2, 2. The charcoal stays in each cooler twenty-four hours. Often a water spray is used in the second cooler. The charcoal is then dumped into shed 3, where it is screened and bagged. At 7, 8 is the boiler house, containing boilers, engines and pumps. In the refinery building at 10 are collecting tanks and settling vats. At 11 are shown the acid and tar stills with condensers. The lime-lee stills are shown at 12, the alcohol tanks at 13 and the alcohol stills at 14. An open oven is shown at Figure 4 and wood cars with charcoal in Figure 7.

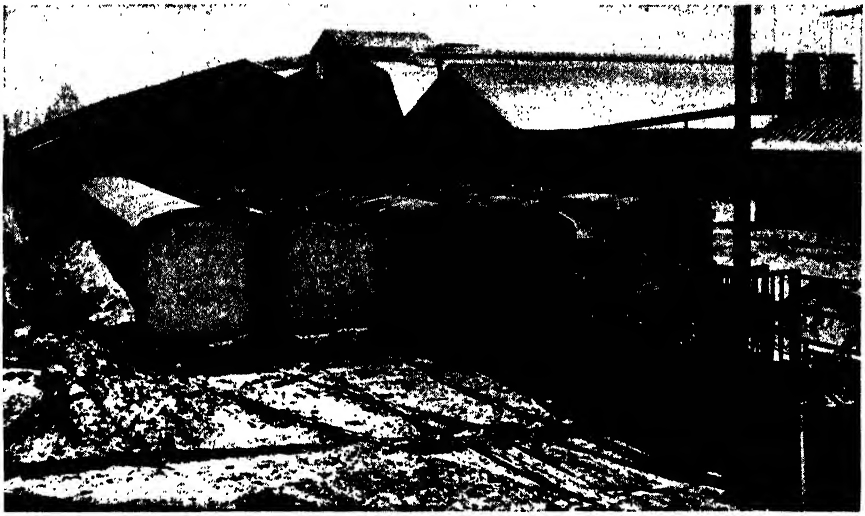

Fig. 7. Buggies for Wood and Charcoal Passing from One Charcoal Cooler to Another. (Courtesy Dr. D. F. Othmer, Polytechnic Inst., Brooklyn, N. Y.)

Yields—From an average cord of seasoned hardwood there is obtained 200 to 250 gal. of pyroligneous acid, containing fatty acids, chiefly acetic acid, varying from 4½ to 7 per cent acid with about 4 to 5 per cent of methanol. There is also some acetone, light oil, metacetone and other ketones, aldehydes and tarry products.

The yields from one of the older oven plants based upon a year's operation were 11.32 gal. of 82 per cent methanol, 173 lb. of acetate of lime and 54 bushels of charcoal per cord of wood. In general, the yields show 8.5 gal. of refined methanol, 200 lb. of acetate of lime (equivalent to 114 lb. of acetic acid) and 48 bu. of charcoal. A new plant claims a consistent yield of 10 gal. of refined methanol and over 125 lb. of glacial acetic acid per cord.

A departure from the older techniques and equipment is found in the Iron Mountain, Michigan, wood distillation plant of the Ford Motor Company[2] which went into operation in August, 1924. The raw material of the plant is

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[2] Nelson, W. G., Ind. Eng. Chem. 22, 312 (1930).

wood scrap and is about 70 per cent maple, 25 per cent birch and 5 per cent ash, elm and oak. The reported yields per ton of dry wood are given in Table 2.

TABLE 2—AVERAGE YIELD OF VARIOUS PRODUCTS AT THE IRON MOUNTAIN PLANT, FORD MOTOR COMPANY, PER TON OF DRY WOOD

Charcoal	600	lb.
Noncondensable gases (290 B.t.u. per cu. ft.)	5000	cu. ft.
C. P. methanol	3.118	gal.
Methyl acetone	0.653	gal.
Allyl alcohol	0.048	gal.
Ketones	0.226	gal.
Methyl acetate	0.945	gal.
Soluble tar	22.0	gal.
Pitch	66.0	lb.
Creosote oil	3.25	gal.
Ethyl acetate	14.65	gal.
Ethyl formate	1.27	gal.

The reported composition of the noncondensable gas is given in Table 3.

TABLE 3—AVERAGE COMPOSITION OF NONCONDENSABLE GAS FROM RETORTS AT IRON MOUNTAIN PLANT, FORD MOTOR COMPANY

Constituent	*Per Cent by Volume, Dry Gas*
H_2	2.2
CH_4	16.8
C_nH_{2n}	1.2
CO	23.4
CO_2	37.9
O_2	2.4
N_2	16.0

REFINING OF PRODUCTS

To obtain the various products, different methods are used according to the degree of refinement required. Some of the products which were formerly made by the destructive distillation of wood are being discontinued owing to improved synthetic processes of manufacture. However, some of the main products still made by this distillation are acetic acid, methyl acetone, methanol, and sometimes gray acetate of lime.

Acetic Acid—Acetic acid made from hardwood distillation amounts to about 10 per cent of the total acetic acid used. It has to be sold where a weak acid can be employed since it occurs in dilute solution. If it is concentrated, it must come in direct competition with synthetic acid.

Acetic acid is used in the manufacture of acetates, particularly cellulose acetate, for which there is an increasing demand. Other uses are for neutralizing and acidifying and in the making of esters. It is also a solvent for volatile oils and a vehicle for carrying out other reactions.

Acetic acid is a natural product of the distillation. However, its manufacture involves the separation of the acid from water, methanol and similar products, and dissolved tars. Above all a cheap method of water removal is necessary. The following methods show the various ways of accomplishing this result.

The Suida Process.[3, 4] This process is based upon the solvent action of a special heavy tar oil distillate upon acetic acid vapors. The vapors from a still enter the base of a scrubbing column and the solvent tar oil enters near the top and comes out at the bottom. The tar oil absorbs the acetic acid and condenses some water, while the methanol, acetone, aldehydes and the remaining water vapor pass out at the top to a condenser.

The tar oil, acetic acid and water drop through a dehydrating tower, from which the water vapor and a little acid are returned to the scrubbing column.

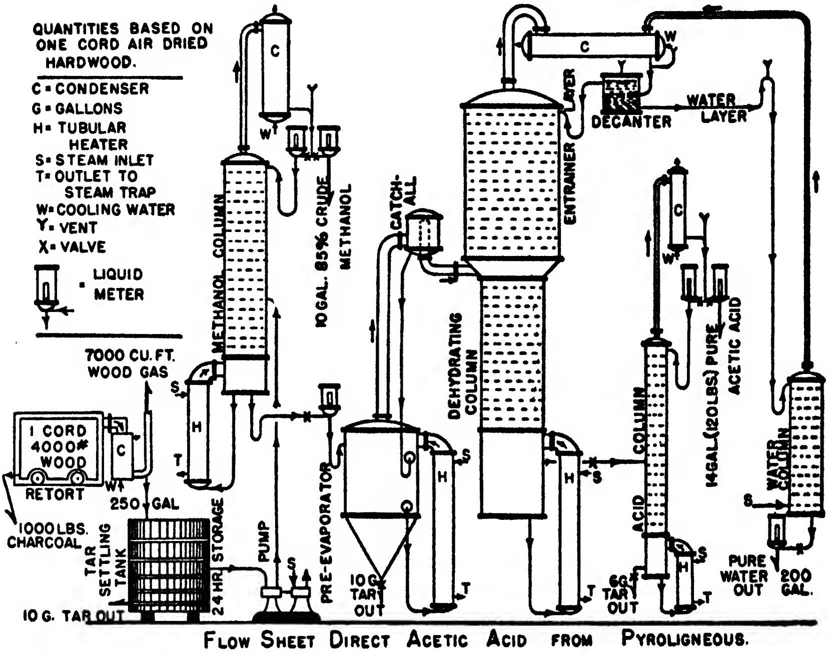

Fig. 8. Othmer Process for Acetic Acid Production. (Courtesy D. F. Othmer)

The remaining acetic acid and tar oil is pumped to the top of a stripping column where the acetic acid and water are separated from the tar oil. They then pass to a rectifying column where the acetic acid and water are partly separated. The strong acid (92 per cent) is bled off from an intermediate plate while the water and some acetic acid pass to a condenser to make a liquor containing about 15 per cent of acetic acid which can be rerun with the pyroligneous acid. The tar oil from the stripping column is cooled and made ready for use again. The process can be used at any hardwood plant starting at the point in the process where the pyroligneous acid is distilled.

Other processes for dehydrating weak acetic liquors depend upon the use of azeotropic mixtures where water is entrained. The auxiliary product should not form a constant-boiling mixture with anhydrous acetic acid and be only sparingly soluble in water, if at all. There are a number of such withdrawing agents, such

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[3] Partridge, E. P., Ind. Eng. Chem. *23* 482 (1931).
[4] Poste, E. P., Ind. Eng. Chem. *24*, 722 (1932).

as ethyl and methyl acetates, ethylene dichloride, isopropyl ether and butyl acetate.

Othmer Process.[5] In this process the weak acid vapors coming from the distilling of the pyroligneous acid are led into a column still, with enough withdrawing agent to form a complete constant-boiling mixture with the water. The vapors are condensed and the water separated by decantation. The withdrawing agent floats on the water.

A specially designed column (practically a chamber column) is used for removing (1) a mixture of methyl acetone and methanol at the top (2) wood oils through the side at an intermediate chamber, (3) dealcoholized liquor near the bottom and (4) tar, at the bottom.

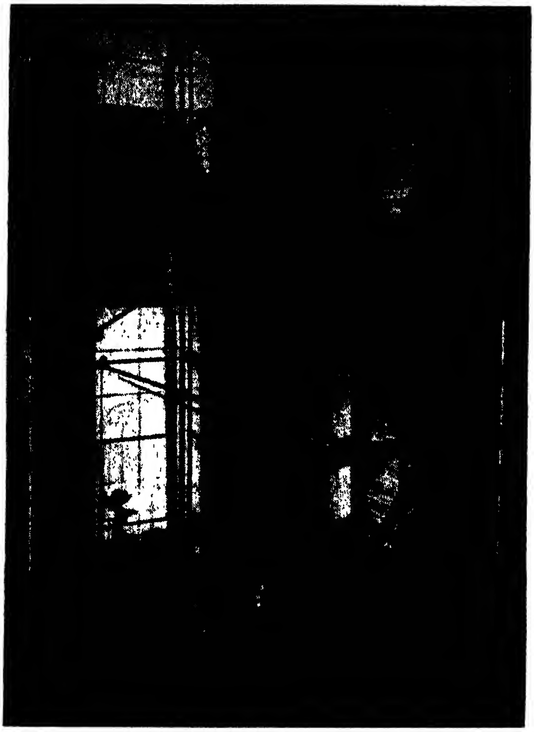

Fig. 9. Dehydrating Still—Othmer Acetic Acid Process. Pre-evaporator—lower right-hand corner. (Courtesy Dr. D. F. Othmer, Polytechnic Inst., Brooklyn, N. Y.)

The dealcoholized liquor is pumped to a pre-evaporator in definite quantity in order to remove the residual tar and to supply water and acetic acid vapors to the second column. See Figures 8 and 9. The withdrawing agent, which is butyl acetate, enters as a reflux at the side near the top of the column. The top chambers of the dehydrating column are wider than those of the bottom, to give

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[5] Othmer, D. F., Trans. Am. Inst. Chem. Eng. *30*, 299 (1933-34); Ind. Eng. Chem. *27*, 250 (1935); Chem. and Met. Eng. *40*, 631 (1933), *41*, 81 (1934); U. S. Patents 1,804,745 and 1,917,391.

the butyl acetate room to mix better with the vapors. The vapors passing through represent the constant-boiling mixture of butyl acetate and water and they are condensed and separated by decantation, the butyl acetate flowing back into the top of the column and the water passing out at the bottom. The butyl acetate is slightly soluble in water so the water is passed through a stripping column to distill out the butyl acetate with a little water, leaving the remaining water to discharge from the bottom, practically free from the withdrawing agent. The vapors from the above are condensed and enter the separator from the column condenser, to be separated with the regular liquor flow.

The anhydrous acid still contains some tarry products, so it is redistilled in a batch apparatus with a rectifying column, to make glacial acetic acid. The residue in the still is composed mostly of propionic and butyric acids. If all empyreumatic substances are to be removed, the acid is distilled with sodium bichromate. In making glacial acetic acid, silver tubes are used in the condenser.

A diagram flow sheet of this process is shown in Figure 8. This does not show the wood oil outlet at the side of the first column. An addition to the process would be column stills for rectifying the crude methanol separated by the methanol column.

Brewster Process.[6] Another type of process for separating acetic acid from water employs liquid-liquid extraction. The solvent has a greater attraction for acetic acid than does water and is also insoluble in water. Isopropyl ether is passed into the bottom of a stripping tower while weak acid is falling from above. The droplets of ether pass upward through the water and take the acetic acid to the top of the tower where it overflows. The water passes off at the bottom and contains but a small amount of ether, which can be distilled out. In the same way the ether is distilled from the acetic acid leaving the acid water-free.

This process is more suitable for dehydrating weak refined acid.

Improvements are being made in column stills. It has been found that entrainment does not hinder the separation of components in a column as much as higher velocity improves it. For this reason columns are being made with special baffles following each chamber, to separate the entrainment, thus speeding up the rate of flow through the column. The use of a spiral, rotating at a high speed, has been suggested as a means for providing a long counter-current path for vapor and liquid.[7]

For a discussion of the principles and types of equipment used in the operations of extraction and distillation discussed above, see Chapter 2, The Unit Operations.

Methanol—The production of methanol from wood has dropped off considerably owing to the competition of synthetic products. The total production of methanol from all sources increased rapidly after the price dropped and new uses were found, but the amount made by wood distilling plants has decreased one-third, whereas the number of plants has dropped over one-half.

As stated before, the pyroligneous acid contains the methanol. It can be removed by distillation, either before or after neutralizing the acetic acid. With direct acetic acid processes, it is removed as the first fraction from the distillation in a separate column with special plates to take care of tar formation in

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[6] Brewster, British Patent 187,603 (1922).

[7] Chem. Ind. *43*, 507 (1938).

the column. Above the feed inlet, bubble caps can be used. A strong alcohol of about 82 per cent can be made, if a bleeder is used on the side of the column to remove the wood oils. When a simple still is used to remove the dissolved tar the acid is distilled and all the vapors collected together after condensation are settled. The heavy oil settles to the bottom and the light oils float on top. These separated oils and the oils obtained after a further distillation of the middle portion are collected, mixed and sold, alcohol-free, as hardwood flotation oils. They consist of creosote, guaiacol, methyl-ethyl ketones and other wood oils.

After neutralizing the clear liquor from the simple still or evaporator, and after settling, this liquor can be redistilled in a column still to make 82 per cent methanol.

To further refine the methanol, a product of 92 to 95 per cent can be obtained easily by distilling the 82 per cent liquor in a batch column still, by separating the distillate into fractions. Usually these fractions contain different amounts of acetone. The constant-boiling mixture of methanol and acetone is found in the first fraction, as it has the lowest boiling point. The middle portion has a small amount of acetone and the third fraction the allyl alcohols and wood oils.

The first runnings of the distillate are more or less colored, but the middle fraction is practically colorless and contains upwards of 92 per cent methanol. After the middle portion distills the methanol begins to contain oil and it becomes non-miscible with water. Subsequently the distillate becomes turbid and finally a mixture of oil and water comes over which separates in two layers. There are methods of removing the last traces of acetone, but these are not much used on a commercial scale.

The refining of methanol in a continuous still presents quite a problem. It is necessary to divide the distillation into three parts. The weak alcohol is freed from heads and oils in one still, the weak alcohol residues passing continuously to another still of similar type. The oils are bled off the side. In the second still, the methanol, and any heads and oils still present are distilled from the water, the water going to the sewer. The oils accumulate at the bottom of the column above the still proper, the methanol is bled off near the top and the heads pass out to the condenser. In the third still, the heads and methyl acetone are distilled from the alcohol, the heads pass to the condenser, the methyl acetone being bled off near the top of the column. The methyl acetone is a mixture of constant boiling point containing approximately 15 per cent methanol and 85 per cent acetone, and it is sold as such.

Some of the sections of the last two columns are arranged so that the liquor and vapors in them can be treated successively with sulfuric acid and caustic soda.[8]

Hardwood Tar—The tar from hardwoods is steamed to recover its content of acetic acid and methanol, and the residue usually burned as fuel. It can be given special treatment if desired. Where the Suida process for direct recovery of acetic acid is used, a heavy distilled fraction of the tar is used as a withdrawing agent for the acetic acid vapor.

To make tar oils, distillation is resorted to and variations can be made in the cuts to suit the properties desired in the fractions taken. Tar is distilled in a

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[8] Robinson, C. S. and Gilliland, E. R., "Elements of Fractional Distillation," p. 238 et seq., McGraw-Hill (1939).

steel still, sometimes provided with a stirrer, which is set in a brick furnace. The still could also be a horizontal cylinder. Heat is applied slowly and the distillate collected until the specific gravity of the tar oil reaches about 0.98, at which time the receiver is changed. Some of the oils present in the tar distill unchanged, while the heavier products are broken up to a greater or less degree, forming pitch, coke, and gas. Following the light oils, a heavier yellowish green oil comes over, having a sp. gr. of upwards of 1.01. The distillation can be carried on until nothing but coke is left in the still, but it is usually better to stop with the production of pitch which can be drawn off hot from the still. The condensate is sometimes divided according to the temperature of distillation; the light oils being collected up to 240 deg. C. and the heavy oils between 240 and 290 deg. C.

If it is desired to make wood creosote, these oils are again redistilled and the heavy oil fractions combined. The heavy oil contains most of the creosote, which is extracted from the heavy oil by means of caustic soda lye of about 1.2 sp. gr. The hydrocarbons are boiled out and the creosote separated by neutralizing with sulfuric acid. The treatment is repeated and the final creosote redistilled, the product coming over between 200 and 220 deg. C. being called commercial wood creosote. To further purify it, it is oxidized with a mixture of potassium dichromate and sulfuric acid and again distilled.

Charcoal—As the charcoal comes from the ovens, it is in lumps, but as it breaks quite easily a great deal of fine material is produced. For domestic use, the charcoal is broken up and screened and placed in small paper bags. In spite of the cheapness and convenience of coal and oil, a surprising amount of charcoal is used as a domestic fuel. Charcoal burns with a hot, clean flame and is especially valuable for camping purposes. It has also been used under certain kind of stills because it makes no smoke for detection by a revenue officer. It is now used chiefly in the manufacture of alloy steels.

Activated charcoal is a different product from ordinary charcoal, as it has improved adsorbent properties. It is usually made by treating ordinary charcoal at a high temperature in the presence of superheated steam. This more completely removes the tarry product thus making it more porous.

Calcium Acetate—Acetate of lime was formerly one of the important products, but is now made chiefly by a few small plants, the larger ones being converted into direct process plants.

To make acetate of lime, the pyroligneous acid is distilled in a copper still before neutralizing and it is thus partly freed from tar. The residual tar amounts to about 5 per cent of the pyroligneous acid. It is pumped to a tar still where the remaining acid is removed by distillation, using heat from a steam coil and also live steam. The settled tar which separates out before the distilling of the pyroligneous acid is usually mixed with the other tar before distilling. The residual tar is known as "boiled tar" and is used for fuel and also for special distilled products. In the Suida process, this tar is distilled and a high-boiling fraction which is obtained is used for scrubbing out acetic acid from the pyroligneous acid vapors.

The condensate of alcohol and acid from both stills is neutralized with lime and settled. Formerly in large plants the custom was to run the neutralized liquor through a continuous column still, heated by a steam coil. The condensed vapors from the condensers were collected in a tank. At smaller plants, the tar-free liquor is distilled in an intermittent steel still called a "lime-lee" sometimes supplied with a small fractionating element. In this still the methanol is separated from the acetate liquor, the distillate containing about 8 to 10 per cent of methanol.

The residual liquor from both the column or the "lime-lee" stills contains the acetate of lime solution, which is allowed to settle in tanks. The clear solution is evaporated to remove the water. At some large plants the water is removed in multiple-effect evaporators, followed by evaporation to a paste in open steam pans. At small plants the liquor passes directly to the steam pan. The paste is removed to the acetate floor on top of the retorts, where the heat of the oven furnace finishes the drying.

At one American hardwood plant, the tar is settled out and the clear liquor is evaporated in multiple effect evaporators and the soluble tar continuously removed. The evaporated liquor is neutralized in batches with milk of lime and settled. The sludge thrown down is filter-pressed. The clear solution is distilled in steam-heated column stills. These stills are capable of giving a distillate of upwards of 90 per cent refined methanol. The liquor coming from the bottom of the still is a solution of neutral acetate of lime. This solution is evaporated in multiple effect evaporators to a thick solution. It is then dried to a mud on an atmospheric drum dryer. This could continue to dryness but on account of the dust, the final drying is done on a belt dryer such as a Huillard, which keeps the acetate in a granular form.

When gray acetate of lime is dry, it is a gray powder containing 2 or 3 per cent of moisture and about 83 to 84 per cent of real acetate of lime.

Acetate of lime was at one time the chief source of acetic acid but direct processes making acetic acid from pyroligneous acid and processes producing it from other materials have cut down almost entirely the use for this purpose. It is still used for other purposes in smaller quantities.

Sodium Acetate—At the present time acetate of soda is made from weak solutions of rectified acetic acid containing about 15 per cent of acid. It is not made at the distillation plant, but could be in connection with direct acetic acid processes. Any copper which is present is precipitated by the addition of a little sodium carbonate, in excess of that required to neutralize the acetic acid. After filtering, the acetate liquor is evaporated in tin-lined vessels heated by steam. A little acetic acid is added to the solution to remove carbonates and the solution crystallized in the regular manner. These crystals are drained and dried by centrifuging or storing in a drying room.

Other Products—There are a number of different products that can be made in small quantities. These are derived from the tars and alcohol residues (see Table 2). The gas, representing 20 per cent of the weight of the wood, is burned under the boiler or retort furnace.

It has been suggested that the carbon monoxide, hydrogen and carbon dioxide of the gas (see Table 2) could be utilized as the raw material for synthesis of methanol and organic acids. This has not been seriously attempted yet, and the economic feasibility is somewhat uncertain.

Pine Wood Distillation—In many respects the raw material for pine wood distillation is different from that for hardwood distillation. Although green wood could be used to advantage, for instance, fat butts of trees or slabs, it is usually the dead down timber and stumps that furnish the raw material for this distillation. The dead wood represents sound wood left after logging operations. It is also known as top wood and "light wood" in contrast to stump wood. Only special grades are adaptable, those pieces known as "fat" wood being the proper kind for distillation. The fatter the wood the heavier it is, and the greater quantity of products that are obtainable. This wood is cut up into four foot lengths or shorter and is split to a maximum of six inches in diameter.

There is a considerable quantity of fat wood in the Pacific States and some in Michigan and other pine and fir districts. However, this material does not contain enough resinous material to justify distilling in competition with the resinous wood of the South.

This southern wood generally comes from long leaf pine, Cuban pine and sometimes a few stumps of loblolly and shortleaf. The supply is not a permanent one. The only renewal comes from the cutting of virgin forests as second growth material is rarely acceptable, but it will take many years to deplete it. The area in which it is found stretches from North Carolina to Texas, ranging mostly one hundred miles to two hundred and fifty miles from the coast.

The value of the raw product is comparatively little. It is sold in the woods by the ton, ranging from 12½¢ on private property to 30¢ per ton on Government property.

The stump wood is often blown out of the ground with dynamite, but recently caterpillar tractors and push-dozers are being used very extensively. The average tractor wood is not as good as the dynamited wood for two reasons, (1) because the small stumps are less resinous and (2) because the blasting of the stump scatters the decayed parts so that they are not picked up. The prepared wood is brought to the factory in trucks or boxcars and commands a price of $2.50 per ton and upwards unloaded at the plant. Top wood having a denser structure is more suitable for charcoal making than stump wood. The chief commercial products obtained by the distillation of pine wood are pine tar, pine tar oil, wood creosote pine oil, turpentine, dipentine and akrol (or pinapp as it is called), and a residue of charcoal.

The yield of pyroligneous acid is less than from hardwoods and contains a lower percentage of acetic acid and methanol. On this account, the pyroligneous acid obtained is not usually saved.

Equipment and Operating Methods—The distillation of pine wood as carried out at the various plants, requires retorts varying in size and shape with the methods of operating and the products sought.

There are several methods of treating resinous woods. The valuable part being the oils and tars, the operation should be carried on with the object of recovering as much of these as possible, at the least cost. The turpentine is present in the wood as such. Some undecomposed rosin is found in the tar and tar oils.

The destructive distillation of resinous wood is carried on in a very similar manner to the treatment of hardwood. So far, both horizontal and vertical retorts have been used varying in cubic capacity from ¾ to 10 cords. Various-shaped retorts have been used, and points of advantage claimed for each one. In addition to the regular steel retorts, concrete retorts heated on the inside by means of cast iron flues have been tried; some holding from ten to eleven cords were successfully operated for a number of years.

There is still a diversity of opinion as to the best way to destructively distill resinous wood. Some prefer a reasonably small retort heated slowly so that the resin will melt and run out of the bottom, any oil vapor coming off at the same time being passed through a condenser. The condensers are similar to those used in the hardwood industry. In such outfits, the ratio of oils and tars varies according to the shape and size of the retort, the method of applying the heat and the time of distillation.

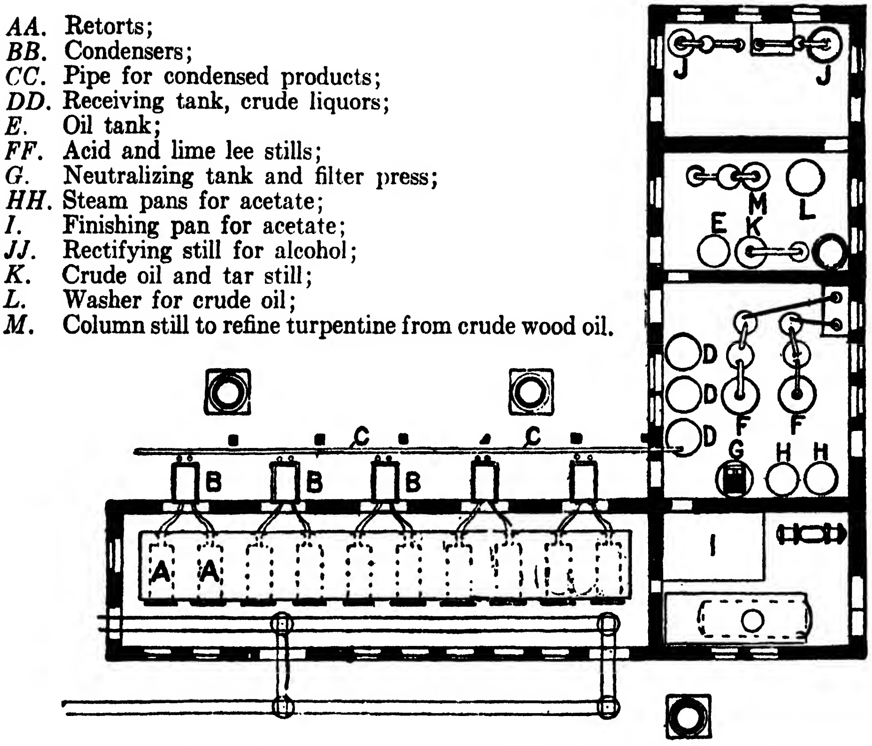
AA. Retorts;
BB. Condensers;
CC. Pipe for condensed products;
DD. Receiving tank, crude liquors;
E. Oil tank;
FF. Acid and lime lee stills;
G. Neutralizing tank and filter press;
HH. Steam pans for acetate;
I. Finishing pan for acetate;
JJ. Rectifying still for alcohol;
K. Crude oil and tar still;
L. Washer for crude oil;
M. Column still to refine turpentine from crude wood oil.

FIG. 10. Plan of Complete Plant for Distillation of Resinous Wood.

Others prefer the small retort, with a distilling period of twenty-four hours or less, with no provision of collecting tar from the bottom. In such cases the rosin and tar distill on the bottom of the retort and the vapors pass upward to a condenser, leaving a tar-coke behind. Such a plant is shown at the left side of Figure 10.

Other operators prefer the large retort with cars on the inside, with the distilling period of approximately thirty hours. Using such retorts it is possible to make a cut of the condensed products. The liquid portion on the bottom of a hot retort is usually black and when cool forms a pitch.

There are a number of other items which are to be considered which also affect the type of retort to be chosen. It is desirable that the resulting turpentine be as uncontaminated as possible, and that the tar produced should have as good a color as possible. The cost of fuel must also be considered. The action of the hot furnace gases on the shell of the retort is very destructive so consideration must also be given to this fact. In addition it must be remembered that wood is a poor conductor of heat and it is practically impossible to distill it in blocks so that all parts will be distilling the same products at one time. Because of all these items, it is advisable to know in advance of construction what particular results are desired before selecting the type of retort to be used.

There are reasons for these various practices based partly on selling requirements and partly on operating conditions. Some of the reasons given by those who use the ¾ cord retort are that it is more easily heated within a given time than a larger one, consequently the retort wear is not as great. Also, the charcoal is supposed to contain less brands, because of less area of the retort being exposed to the air. On the other hand, those who use a larger retort (twice as large) state that the retorts and furnaces cost less per cord to construct, so that the wear and tear is no greater than for the smaller retorts. The labor cost of handling is enough lower, to offset any possible extra cost for depreciation as compared with smaller retorts.

Those who use the very large retorts with auxiliary equipment, claim a saving in the cost of both fuel and labor.

The use of internal flues is principally to prevent the action of the furnace gases on the retort shell. There is also a saving in furnace construction. Because of the smaller heating surface, the temperature in the flue must be higher than that in the flue of the other type of construction when the retort is heated from the outside of the shell. It is possible that flue expense and delays may prove as great as the expense attached for this reason to the other type of retort.

The considerations for using a vertical retort seem to be the possibilities of making better quality products with less expense. If the tar comes out at the bottom as is usually the case, it does not have to come into contact with the hot retort shell. When using vertical retorts, the custom is to draw off the tar from the bottom and to fractionate the vapors by making cuts at the tail pipe of the condenser.

Kiln tar made in pits seems to have a readier sale at a higher price than retort or distilled tar. The small retort heated slowly makes a tar that approaches kiln tar in color and other properties and it is for this reason that some prefer this equipment.

The small iron retort heated by internal flues has proved to be a failure, partly from poor construction and partly from lack of heating surface. These are the so-called "portable retorts."

As there are successful companies using different types of retorts, it is evident that business considerations are more responsible for success than types of process. It is not surprising that with such diversity of operation, there is nothing standard in the industry.

It is obvious from this brief discussion of requirements, that operation in this field is still very much of an art rather than a carefully controlled and completely understood method of manufacture.

Products of the Distillation—With all types of equipment, the distillation is accompanied by phenomena similar to those occurring with hardwood distillation. Upon the application of heat, the water, accompanied by some of the turpentine and other oils present in the wood, distills off. As the temperature increases, some rosin distills over with the oils, particularly if steam is still present. After most of the water has been expelled, the wood fiber begins to break down, similar to the action with hardwood, similar products being produced. Pyroligneous acid is found in the distillate, with oil and rosin solution floating on the top. As the distillation continues, gas is formed and the rosin begins to break down. The oils collected up to this point are sometimes called "sweet crude" and collected separately. The remainder of the distillate is called "destructive crude." This contains the remainder of the pyroligneous acid and wood oils from the distillation of the wood as well as the oils from the distillation of the rosin.

If the tar is not drawn off at the bottom, the rosin, creosote and oils contained therein, distill and the tar becomes darker and darker until it becomes pitch. If the pitch is not drawn off, the distillation continues and the pitch is converted into coke. The residue from the distillation remains in the retort as charcoal and tar coke. Gas is formed as in the distillation of hardwood. Overheating causes more gas to form, with corresponding loss of oils. The gas, after passing the condenser, often contains a light oil which is sometimes scrubbed out. In large plants, the gas is piped to the boilers or retorts and used for fuel, whereas in the small plants it is often allowed to escape to the air.

The condensed oils and acid have similar specific gravities. When warm, it is usually possible to separate by gravity. Upon long standing the oils will come to the top. Separation is then readily effected. When emulsions are formed separation is difficult. In those cases where the tar is drawn off at the bottom of the retort during distillation, the tar usually contains a large amount of acid water. This acid water often separates in part by gravity, but its complete removal is very difficult. By steaming slowly to avoid too much frothing, the water can be entirely removed. All these operations should be carried on in wooden, copper, or cement-lined vessels when acid is present.

Refining the Products—The refined products of the distillation of resinous woods are light oils, turpentine, dipentine, heavy turpentine, pine oil, tar oil, and pine tar. Charcoal is the residue.

The refining of destructive oils is a variable operation because of the diversity of methods of production. At those plants where tar and oil are all distilled and collected together, the resulting crude oils usually float on the surface of the pyroligneous acid. This crude can be sold as such for flotation purposes and has proved to be a very satisfactory product for the purpose. It has been called by various names, but, at present, the tendency is to call it "crude oil of pine wood, or total crude" and pine tar oil.

This crude oil contains light oils from the wood and rosin, the turpentine and pine oils, the creosote and tar oils and the rosin oils and tar. It is customary to remove the light oils, turpentine and pine oils by a rough separation in a steam-heated still, a live steam jet being used in conjunction with a coil. The light oils are collected separately. The residue left is called "crude tar oil." This is removed to a still heated by direct fire and the creosote and refined tar oils removed. The tar remaining in the still is known to the trade as "retort tar." The whole separation is sometimes done in a fire still.

The light oils are redistilled once and the distilled oil sold as solvent oil under various trade names. The crude turpentine and pine oil fraction is treated in a mixer with small quantities of concentrated sulfuric acid, then removed to a steam still and distilled over caustic soda solution. Fractions are taken off and collected separately. The turpentine and also the pine oil are distilled a second time over caustic soda solution and the refined oil collected within the limits of purity desired.

The residues from the stills are often neutralized with pyroligneous acid and the soda creosote which is recovered is sold as a flotation oil.

Most of the steam stills are supplied with some form of fractionating column which makes it possible to make a closer separation than in a simple still.

Where the distillate from the retort is divided into "sweet crude" and "destructive crude," the destructive crude is treated as above, whereas, the "sweet crude" does not need the treatment with acid.

Light Oils. The light oils are known by various trade names such as akrol, X oil, solventine, solvent oil. Sometimes they are redistilled several times. They are then known as XX or XXX oil according to the number of distillations.

Destructively Distilled Turpentine. This is a turpentine whose properties in the main resemble those of gum turpentine or steam-distilled turpentine.

Tar Oils. There are a number of oils that go by the name of tar oil and pine tar oil. Genuine tar oil is a redistilled product, not often made. The total crude coming from the condensers is often called tar oil. Sometimes, the name is applied to a fraction of this distillate. Then a mixture of pine tar and lighter oils is sometimes called tar oil. Probably, a product intermediate between the light oils and pine tar should be called tar oil.

Retort Tar. Pine tar made in retorts is called retort tar. If drawn off the bottom of the retort, it is sometimes called a heavy tar. The tar which is distilled over from the retorts is mixed with the lighter oils. If these lighter oils are distilled from the mixture, the residue is pine tar. If the distillation is continued, the tar can be distilled down to pitch or coke, depending upon the amount of oil removed.

TABLE 4—GENERAL SUMMARY OF REFINED PRODUCTS

Product	*Specific Gravity*	*Distilling Range ° C.*	*Refractive Index*	*Viscosity*
Total crude	1.019	70–345	1.525	2.9
Crude pine oil	.911	70–232	1.489	1.1
Refined pine oil	.910	180–220	....	..
Crude wood turpentine	.887	65–217	1.456	.9
Refined wood turpentine	.865–7	140–180	....	..
Heavy pine-tar oil	1.063	165–350	1.557	..
Commercial pine-tar oil	1.04	180–360	....	..
Light solvent oils	.862	60–190	....	..
Refined tar oil	....	......	....	..
Refined wood creosote oil	.965	105–275	1.5096	1.7
Soda creosote oil	1.025	190–360	1.4977	2.9
Retort pine tar	1.065	207–360	....	..

NAVAL STORES

Naval Stores was the term used to designate the supplies used by the Navy in the days of wooden ships. They were used in painting, caulking and other repairing. In addition, pine tar was used for making rope of which large quantities were then used. The term has been defined by the Federal Naval Stores Act as to comprise the four types of turpentine, namely, gum turpentine, steam-distilled turpentine, destructively distilled turpentine and sulfate turpentine; also gum and wood.

The nomenclature which has grown up around these products is sometimes rather confusing. It reflects the genius of an art rather than a science. In general, however, it can be said that "gum" refers to the turpentine or rosin, obtained from the liquid which exudes from incisions in trees such as the long-leaf or slash pine, whereas "wood" refers to these same products obtained from the destructive or steam distillation of wood.

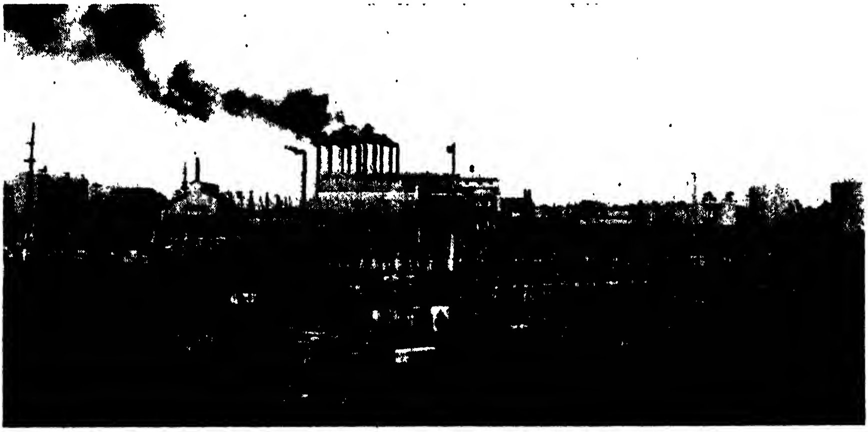

FIG. 11. Steam and Solvent Wood Rosin Plant.

The raw material for the manufacture of wood naval stores is the same as for pine wood distillation.

The wood is handled in practically the same manner to prepare for loading on trucks, except that pieces 18" in diameter and up to 6' long are used. The delivered price for the wood is graded from $2.50 per ton upwards.

The Extraction Process—This process is usually called the Steam and Solvent Process. Much ingenuity has been used to devise suitable mechanical arrangements for carrying it on successfully. The requirements are a wood chipping and elevating system that will deliver the ground wood to the extractors, an easy method of discharge for the wood from the extractors, and the proper discharge system to remove the discharged chips to the boilers or fuel house.

Of all the proposed methods for producing valuable products from resinous wood, the extraction processes seem to promise the best utilization of raw material. The oleo-resins contained in resinous pine and fir wood seem to consist of light oils, heavy oils and resins. The light oils correspond closely with turpentine, the heavier oils or pine oils seem to be oxidation products, chiefly terpineol, and the resin mostly colophony. The presence of small quantities of other products has a marked effect upon the physical properties of the chief ingredients, particularly the odor. At the present time the oleo-resins seem to be the most valuable products of the extremely resinous woods, although pulp and paper are being made from the less resinous wood, and fiber board[9] from the residual chips. The operation of a steam and solvent plant consists in grinding the wood by means of a hog and shredder until it is in a fine granular condition. The comminuted wood is conveyed to a series of pressure extractors. In these it is first steamed under pressure to remove the turpentine and part of the pine oil. Pressure is necessary in order that the live steam and heat may penetrate the mass of the wood. Some plants use as high as 60 lb. per square inch, gauge pressure. The introduction of a lighter boiling solvent than hitherto used, which can be separated from turpentine by fractionation, has made it possible to omit the first step, that of steaming for turpentine from the wood. This solvent is admitted to the extractor containing the ground wood, extracting all three products together.

After removing the oils and reducing the pressure sometimes below atmospheric, solvent is pumped into the extractors to dissolve the rosin and remove the remaining pine oil. The solvent solution is strengthened in rosin content by sending it in series through a number of extractors. In this system the nearly exhausted wood is brought into contact with fresh solvent, which extracts a large part of the remaining rosin.

The rosin solution from the extractor containing the strongest solution is pumped to the washers. The weakest solution is pumped from one extractor to the next. The washed wood is allowed to drain and the drainings pumped out.

Rosin and Solvent Recovery—To recover the solvent from the wood, an operation similar to that for turpentine is required—that of heating and steaming with live steam. At first, but little steam is required owing to the large quantity of light solvent remaining in the wood. To remove the heavier portion, pressure and prolonged steaming are required, to prevent excessive loss of solvent by its remaining in the wood. This last operation is sometimes performed in rotating horizontal cylinders. By this means, the steam is prevented from following channels in the wood chips, as might happen with upright extractors. All the solvent is not recovered, the loss being one of the chief items of expense attending the operation. Several processes have been developed to extract the rosin, varying from one another in some details, but all based on the solvent power of some alkali or volatile oil. The alkali process consists in dissolving the resin in soda solution and neutralizing the solution with acid to regain the rosin. This was tried on a semi-commercial scale but abandoned in favor of the volatile solvent process. When solutions of alkali are used a substance called "humus" is extracted with the resin. It is only recently that a method has been found of separating this from the rosin. The suggested improvement in the alkali process is the use of ammonia as a solvent. The rosin is dissolved from the wood as with other alkali, in the form of resinate. It is claimed that by simple heating without the use of acids, the ammonia is distilled, leaving the rosin and "humus" behind. The rosin is dissolved in gasoline, in which the humus is insoluble. It is further claimed that there is no loss of gasoline. Rosin of good quality can also be steam-distilled direct from the wood when the heat is properly controlled. The method of extracting with volatile solvents has been known for a long time, but the low price of rosin

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[9] See Chapter 37, Paper.

prevented its successful application. Then for a few years the price of rosin was so high that the successful development of the process became a commercial fact, but a slump in value of the rosin and turpentine caused most, if not all, of the plants to close down. With the increase in value of these products most of these plants have resumed operations.

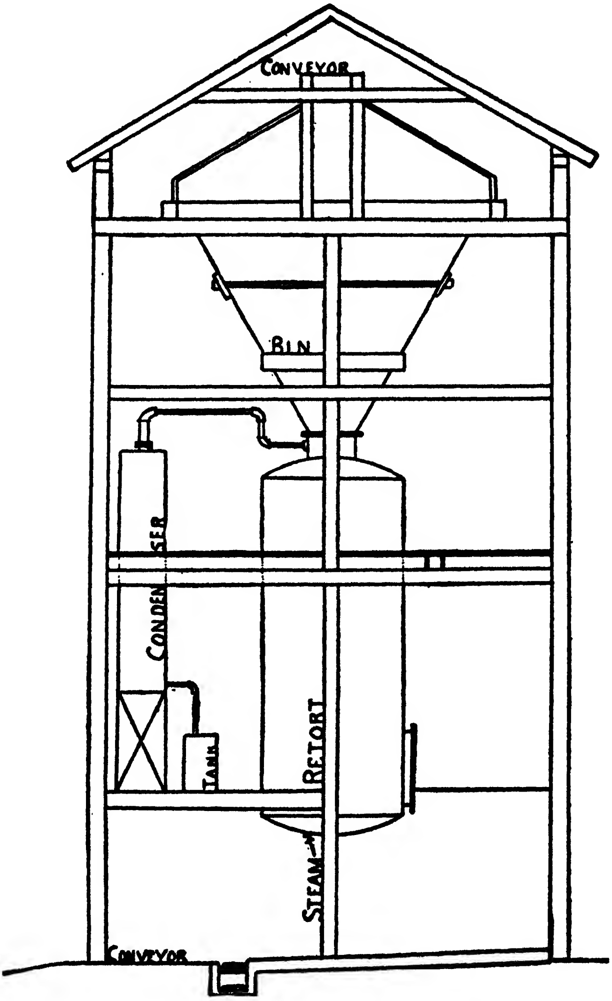

FIG. 12. Diagram of Extractor and Condenser Steam-solvent Plant.

Equipment Used in Processing Operations—A diagram of the equipment used in steam-solvent plants is shown in Figure 12.

In the washers, the rosin solution is cooled by a water spray jetted into the oil. This cools the solution and there is thus precipitated an impurity that would make the rosin of poor quality if it remained. This impurity is spoken of as "nigre." It darkens the rosin and also causes fine black streaks. The rosin solution is passed through several of these washers and finally settled before entering the evaporators.

The equipment for the recovery of the solvent and rosin varies with the emplacement of the evaporators. In some of the plants a horizontal evaporator is used, while in others, the tubes of the evaporator are set in a vertical or inclined position.

These evaporators are sometimes divided into as many as three sections. In one section the solvent is taken off and condensed; in the middle section, the remaining solvent with the turpentine and some pine oil are removed and condensed and in the third section, the remaining pine oil and some resene are removed. In each section, the part not distilled falls to the bottom and is pumped to the next section. The residue from the last section is rosin and this is pumped through steam jacketed pipes to the barreling shed where it is barreled hot. The oils from the condensers are pumped to collecting tanks ready to supply the stills. The evaporators are best operated under a vacuum. When the evaporator has only two sections, the solvent is taken off in the first one and the oils and resene in the other. A sketch of a two-stage evaporator is shown in Figure 13.

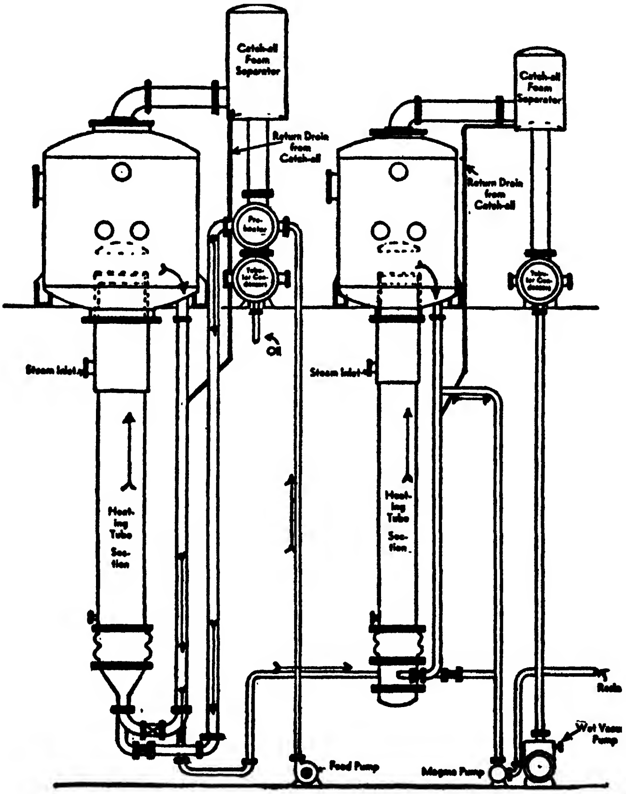

FIG. 13. Two Stage Rosin Solution Evaporator. Modified Swenson Type.

A modification of the process is to finish the rosin to the proper degree of hardness in a still. The residuum from the evaporator is left soft and the final oils removed by distilling until the rosin is of the particular hardness desired. This is probably the surer way to make a rosin of uniform melting point, but it increases the possibilities of darkening the rosin and also its tendency to crystallize.

Refining the Oils—When crude turpentine is made by steaming the wood chips, it is colorless when the first portions are condensed, but the latter portions are quite yellow. The yellow color is due to the presence of crude pine oils and a little resin which distills over with the turpentine. The stills can be worked with live steam without a vacuum, but the present practice seems to favor distilling under a vacuum without steam until the turpentine and dipentine are removed. This is determined by the specific gravity of the distillate. The residue in the still is then dropped into a collecting tank from which it is pumped into another still to refine the pine oil.

When the turpentine contains solvent, the solvent distills first and is collected by itself, then an intermediate fraction is collected containing solvent and light turpentine, after which the turpentine and pine oil remaining are separated.

At some plants dipentine is made. This is a common terpene, but has a peculiarity of having a relatively high boiling point and low gravity. While the turpentine is distilling in a column still under a vacuum, toward the end of the turpentine range the condensate rather suddenly begins to become lighter in gravity. This is the dipentine fraction. This is not pure but is mixed with some turpentine and pine oil fractions. This oil is redistilled to make a fraction conforming to definite specifications.

At one large plant using a light naphtha solvent, the heavier oils coming from the evaporators are distilled under a vacuum and the following cuts made.

Sp. Gr.	
0.733 to 0.765	Naphtha
0.765 to 0.854	Middlings
0.854 to 0.851	Turpentine
0.851 to 0.863	Dipentine
0.863 to 0.940	Light pine oil
0.940 to Finish	Heavy pine oil
Residue "Foots."	

The naphtha is returned to the system for re-use. The middling cut is redistilled to separate more naphtha and turpentine. The turpentine fraction is sold as such or specially refined with alkali and redistilled. The pine oil fractions are distilled over caustic soda and cut so that the water white fractions will have the required gravity. These fractions are dehydrated by heating, to distill the water. Some oil comes over with the water and is saved. The water is easily removed if a vacuum is used. The residue of "foots" is placed in steam-heated tanks or drums and if not sold, it is used for fuel.

REFINED PRODUCTS

Steam-Distilled Wood Turpentine—Turpentine produced by the above process closely resembles gum turpentine, except for the odor. The odor of gum turpentine is supposed to be due to an aldehyde which has no commercial value. The odor of steam-distilled wood turpentine is due to the different oils contained therein.

Steam-distilled turpentine contains pinene, both alpha and beta, also in much smaller quantities, limonene, dipentine and some terpinene. Most of these can be produced from pinene.

Dipentine—It has been stated that this oil is found in the intermediate fraction between pinene and pine oil. The oil is redistilled and the light and heavy ends cut out and the middle fraction used as dipentine.

Pine Oil—This is a valuable oil that was discovered as one of the products of the distillation of pine wood with steam. At first no use was found for it, but gradually its intrinsic value became known and it has found many uses.

Soluble pine oil is a solution of pine oil in a special soap solution. Using freshly distilled pine oil and a recently made solution, the phenol coefficient (action on typhoid bacilli as compared with phenol) is around 5. It quickly loses this value, however, and becomes less effective.

Pine oil containing as it does an alcohol (terpineol and other terpene alcohols) has a tendency to neutralize the effect of carbolic acid on the skin.

Steam-distilled pine oil is considered the best flotation agent in the recovery of some metals from their low-grade ores. It is used for making terpin hydrate by treatment with 5 per cent sulfuric acid. It is much used as a solvent. Large quantities are used in the soluble form for making disinfectants and for cleaning oil from cotton yarn and cloth.

There are several grades made depending upon the gravity and color. The standard grade has a specific gravity ranging from 0.933 to 0.938. The color ranges from water white to almost red. The two grades usually sold are the water white and light amber. The water white is made from the amber by redistilling with or without caustic soda. The special grades are made by varying the gravity.

The crude pine oil from the turpentine still is collected until enough has been accumulated to make a charge for the pine oil still. This still is the same size as the turpentine still and is operated in a similar manner under a vacuum. Live steam is used and the oil is distilled until the color becomes too dark to be merchantable and the residue is drawn off as "foots." This is a semisolid substance of a sticky nature comprised of resene, a little pine oil and usually a small amount of rosin.

The collected pine oil is wet, that is, it is capable of absorbing about five per cent of water, which is difficult, if not impossible to settle out. By heating the oil in a simple still, preferably under a vacuum, the water and some oil distills, leaving the remaining oil free from water.

For standards and methods of testing these various materials see the standard methods of the American Society of Testing Materials.

Wood Rosin—Although wood rosin closely resembles gum rosin, it has different characteristics.

Ordinary FF wood rosin when powdered has a yellowish cast, whereas, gum rosin of any grade shows white under similar conditions. The purer the wood rosin the less this yellow shows.

Most grades of wood rosin have a larger percentage of resene, as the nonsaponifiable matter is called. The amount of this varies with the hardness of the wood rosin. If the rosin is steamed long enough, when finishing, a considerable quantity of this unsaponifiable material is removed.

Wood rosin seems to have a tendency to form crystals which make it opaque. This may be due to a less soluble form of abietic acid or because too much solvent has been removed. As this kind of rosin has a higher melting point than the clear rosin, the lack of solvent may account for the crystallization. A trace of water will sometimes cause this, probably by starting crystallization from a super saturated solution. It may be due, also, to the formation of isometric crystallizable bodies such as d-pimaric acid.

By the capillary method, the melting point or softening point of wood rosin ranges from 53 to 55 deg. C., whereas gum rosin varies from 50 to 70 deg. C. A strongly-crystallized wood rosin showed a melting point of 75 deg. C.

In addition to softening point, color, acid number and saponification number are important quantities in determining rosin quality.

It is claimed that rosin which is highly dextrorotary is less apt to crystallize, so the optical rotation is often determined.

Wood rosin, although an amorphous solid, will dissolve linoxylin when melted with it. For this reason it is much used in the manufacture of linoleum. Even when it is in solution in oils it will dissolve substances which are not soluble in the oils alone.

On account of its physical and chemical properties, rosin is used[10] in such industries as soap making, paper making, sealing wax, varnishes and the like.

REFINING OF ROSIN

There are a great many patented processes for the removal of the dark color from rosin. Very few of them actually decolorize to any great extent without the use of excessive amounts of outside material and with a poor yield of refined rosin. The production of a high grade rosin from FF wood rosin is not so simple an operation as it might seem. The color is not due to a small quantity of a color body having a high tinctorial value, but to a relatively large amount of a color body of low tinctorial value. This means that the removal of the color bodies causes a large loss in weight of the original rosin. This amounts to as much as twenty-two to twenty-five per cent in the manufacture of pale grades.

Wood rosin can be decolorized in various ways. By dissolving the rosin in certain solvents some of the coloring matter remains undissolved. By this method the color can be much improved, but only with the use of solvents difficult to handle on account of extreme volatility. Another method is to filter the rosin in solution through fuller's earth or activated carbon and a third method is to treat the rosin in solution with another solvent which is partially or wholly immiscible with the first and also has a selective action on the color body. By this method, the color bodies leave the rosin solution and are taken up by the added

[10] A complete list of the uses of turpentine and rosin can be found in Gamble, T., "International Naval Stores Year Book for 1940-41," pp. 81 et seq. For further discussion of such uses see Chapter 37, Chapter 43 and Chapter 25.

solvent. By distilling off the first solvent containing the decolorized rosin, the refined rosin will be left as a residue and by distilling off the second solvent, the coloring matter is left as a residue.

Rosin being such a cheap commodity, the use of more expensive agents to clarify it makes it necessary to recover these agents at low cost or the operation fails financially. At the present time, only two methods are in actual use. One is based on the adsorptive action of clays such as fuller's earth and the other is a dual solvent process using petroleum naphtha and furfural.

The Clay Process—This process is carried out as follows: The rosin solution from the extractors is washed and evaporated in the usual manner to make FF rosin with less than 1 per cent of pine oil remaining. The FF rosin is mixed with hot naphtha and the solution is cooled in washers. The cooled washer solution is pumped through towers or vessels containing fuller's earth or magnesium silicate. These are arranged in a series; preferably of three adsorbing, three washing and three reclaiming and repairing. All equipment is made of a material that will not discolor rosin, such as aluminum or stainless steel.

The head tower contains reclaimed fuller's earth or a fresh supply; the third tower is being filled with the raw solution and pushing ahead into the second tower and finally into No. 1, containing the fresh earth. The liquor coming out of No. 1 can be made of any grade, depending upon the relative amount of rosin solution passed through as compared to the amount of fresh clay. When the clay in the back tank is sufficiently saturated with adsorbed material, the whole system is advanced one tower and the back tank cut out for reclaiming and revivifying the fuller's earth.

The reclaiming is done by displacing the raw liquor left in the tower by cold naphtha. The coloring matter is only slightly soluble in cold naphtha. To remove the naphtha, it is displaced in turn with hot alcohol, usually mixed with some naphtha. In spite of the presence of the naphtha, the alcohol dissolves the coloring matter. The alcohol and pigment solution is washed out in a series of towers, by means of hot naphtha. When the alcohol has been washed out, the tower contains the naphtha which can then be replaced with raw rosin solution and the cycle repeated. Or preferably it is made the head tower in the adsorbing series and decolorizes the partially decolorized solution coming from the preceding tower.

The clarified solution is sent to an evaporator to remove the naphtha until the solution is concentrated, when the remaining oil is removed in a pot still for finishing to the desired hardness. The alcohol pigment solution is distilled in fractionating stills to separate as much as possible the alcohol from the naphtha. The mixed alcohol and naphtha solution condensed, which does not separate into layers, is used to extract the coloring matter from the clay.

The above system requires the use of a number of intermediate tanks in order to take care of the fluctuations in the operations.

Although certain details of this process have been covered by a number of patents, the basic principle of the clarification of rosin solutions by means of fuller's earth and activated carbons has been known for a long time.

Selective Solvent Processes—Although the use of a great many substances for clarifying rosin solutions in admixtures of other solutions has been patented, only a few of them have properties required for refining rosin economically. A process of this kind now in operation uses furfural as the selective agent.

If a mixture of petroleum naphtha, rosin and furfural be heated together in definite proportions, the result will be a homogeneous mixture which upon cooling will separate in two layers. The upper layer will contain most of the rosin and naphtha with a little furfural and the lower layer will contain most of the coloring matter, some rosin and the remaining furfural, which will contain some naphtha dissolved in it.

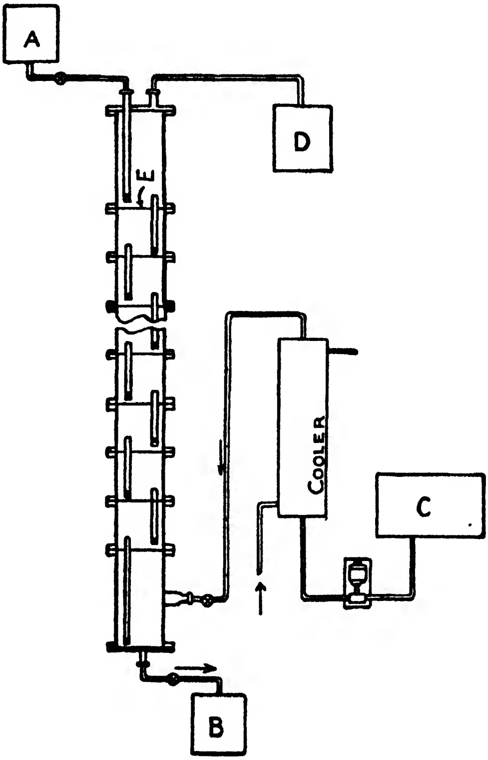

Fig. 14. Counter Current Extraction Tower for Rosin Purification. (Designed by D. A. Lister, U. S. Pat. WO 2,054,432)

A—Refining substance
B—Used refining substances
C—Unrefined rosin solution
D—Refined rosin solution
E—Close-meshed wire screen

From these facts a liquid-liquid extraction[11] system was devised by means of which the furfural and rosin solution in petroleum naphtha are brought together in a continuous manner.

Use is made of a column with perforated plates, similar to a beer still, but with very minute perforations. The rosin-naphtha solution being lighter is intro-

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[11] For further discussion of the principles of the unit operation of liquid-liquid extraction, see Chapter 2, The Unit Operations.

duced in a chamber near the bottom, high enough to allow the incoming naphtha to separate from the descending furfural. The furfural goes in at the top and descends to each chamber through overflow pipes, while the naphtha solution rises through the perforations in the plate to mix with the descending furfural. The rosin naphtha solution flows out at the top and is collected, while the furfural and color bodies are removed from the bottom. The colder the solution the better the separation of naphtha and furfural. A diagram of the type of column used is shown in Figure 14.

By distilling the clarified rosin solution either in an evaporator or still or a combination of both, the refined rosin is recovered. A similar procedure with the furfural solution leaves the color bodies and some rosin as a residue. This residue is sold under the name of "B Wood Rosin." The margin of profit in the operation is decided by the financial returns from the sale of this grade of rosin.

Hydrogenated Rosin—Processes for the hydrogenating of rosin acids have been patented by a number of different men. All of them seem to be based upon the catalytic action of hydrogen and a base metal upon the rosin in solution or in a melted condition.

The only one in use is that of Humphrey,[12] and the resulting product is sold as "Staybelite."

Early patents showed the possibility of hydrogenating rosin acids by means of base metal catalysts. There has not been an extensive demand for hydrogenated rosin so the development of the process has been slow.

The Humphrey process is similar to the earlier processes, except higher pressures are used in order to obtain a greater yield. Of the thirty-one claims in the patent, the essential distinction is that the previously prepared rosin is to be treated with hydrogen under a pressure of 200 to 15,000 lbs. per sq. inch and at a temperature of 275 deg. C. to 325 deg. C. in the presence of an active base metal catalyst for a period of time (0.2 to about 3 hours) until the rosin is at least 50 per cent saturated with hydrogen.

A plant constructed for manufacturing hydrogenated rosin is now producing this product on a commercial scale.

GUM NAVAL STORES

The distinction between wood naval stores and gum naval stores lies in the fact that the gum naval stores products, turpentine and rosin, use the gum which exudes from a wounded pine tree as a source of raw material for the distilling operation. Those trees are selected which will yield enough gum when tapped to justify operations. Such trees are the long-leafed species and the Cuban pine often called slash pine.

At one time, vast forests covered the South, ranging in expanse from North Carolina to Texas. The operations started in North Carolina and moved steadily westward as the supply of trees became reduced. While the supplies in the western section were being utilized, the Georgia and Florida trees reproduced. The stand of trees in the western area of the South is so limited that the main operations are now in the areas that have reproduced. It is possible, that within the

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[12] Humphrey, I. W., U. S. Patent No. 2,113,808.

Georgia-Florida area, proper conservation methods will assure a perpetual stand of trees great enough to supply the domestic needs for naval stores for all time.

Methods of Obtaining the Gum—The methods of operating are very simple and have been practiced without material change since their beginning. But very recently, improved methods have been introduced which are proving of benefit to the producers and to the sellers.

A summary of all improvements tends to show that the best method of obtaining turpentine and rosin from the live tree consists in the use of the cup and gutter system, light chipping and regulated distillation.

To start a tree to producing, the bark is removed about ten or twelve inches from the ground and a space about 12 to 16 inches wide is made by cutting away a little of the wood. An angular cut (V) is made on this surface in which is inserted a metal gutter or apron. Under the gutter and close up to it is fastened a cup made of clay or metal and this is fastened to the tree by a zinc nail or wooden peg.

Two gutters are used on each face, sloping towards each other. The upper and shorter gutter is separated at its lower end about 1 inch or so from the lower gutter and empties into it. The bottom end of the lower gutter extends beyond the end of the bottom of the upper gutter a couple of inches and the gum from both gutters flows into the pot or galvanized box beneath.

The wounding of the tree causes it to exude the resin or gum and this flows on the surface to the gutter and finally into the cup. The gum is highly viscous and soon stops flowing. A fresh incision is made each week forming a V-shaped face. This is called "chipping." Formerly, this streak as it is called was made quite wide and deep, but it has been found that a streak not over two-thirds of an inch wide and not very deep is sufficient. By the end of the season considerable face has been exposed and the gum has to travel over the surface of the wood to reach the gutter. Much turpentine is thus evaporated and the gum takes up coloring matter from the wood. Sometimes a streak is jumped leaving a ridge of wood for the gum to flow over. This gives a straight drop to the gutter without touching the surface of the face below. Because of the viscous nature of the gum and the effects of the wind, this device is not wholly successful. It is better to move up the cups.

At the beginning of a new season, the cups and gutters are moved up the tree, so that the gum will not have to flow over the face produced by the operations of the preceding year.

The gum is dipped out of the cup (called "dipping") into a small bucket and then put into a barrel in which it is hauled to a still. At the end of the season, the material covering the face (called "scrape") is removed in bulk. This contains pine needles, dust and trash which it has collected from the air during the season.

Distillation of the Gum—The distillation is carried out in a copper still connected by a cap and arm to a condensing worm or coil in a tank containing water. Some of these stills have two openings, one for the admission of the gum and the other for the exit of the turpentine vapors. Others have only one, in which case the vapor cap is removed to admit the gum and replaced when distillation begins.

The chief improvement in distilling methods has been the use of the thermometer to regulate the firing, thus doing away with the "sound" method by listening to the variation of the sound at the end of the vapor pipe. Another improvement is the use of the "nursing bottle" with which to catch samples from which the amount of water to be used can be determined.

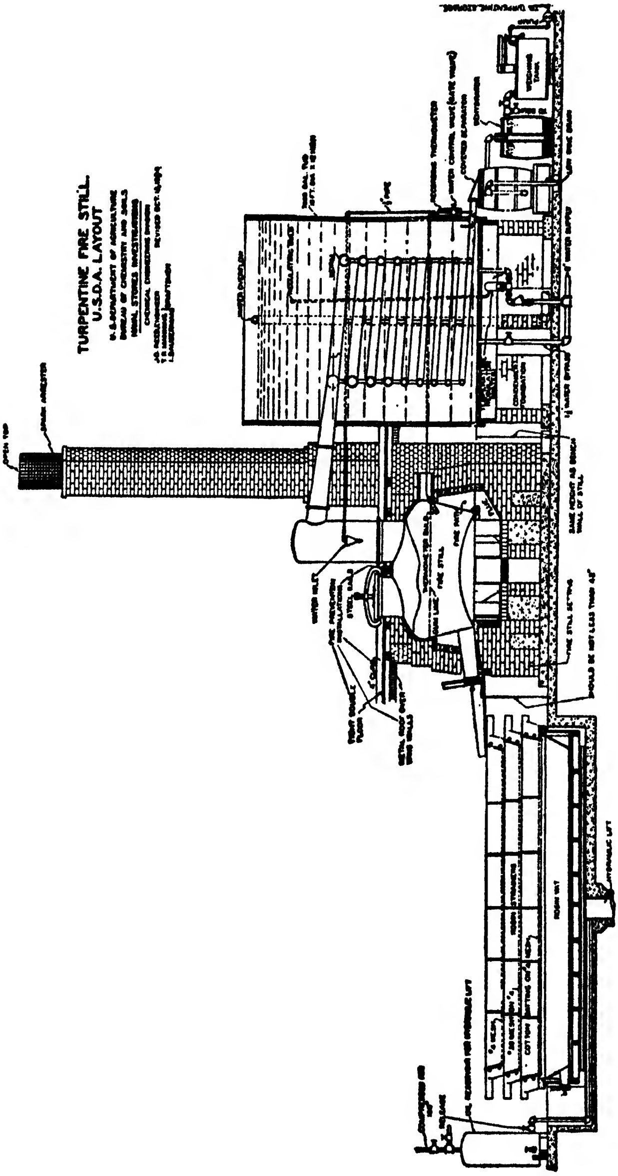

Fig. 15. Turpentine Fire Still. U.S.D.A. Layout.

After the gum has been sufficiently heated, some of the chips and straw floating on the top are skimmed off and the opening closed. By avoiding too rapid heating at the start and also by adding water soon enough, both of which conditions can be determined by the thermometer, overheating and carbonization are prevented and a better grade of rosin is produced.

The hot water coming from the top of the condenser is allowed to flow into the still. This reduces the distilling temperature. The water distills over with the turpentine and both are condensed and collected in a barrel or tank. A barrel is usually used for a separator. This is shown in Figure 15. The oil overflows at the top and the water through a goose neck pipe from below. Sometimes, the oil is passed through another barrel containing dry salt which removes the traces of water that remained in the oil. This is called a "dehydrator."

When most of the turpentine has been distilled, the flow of hot water from the condenser is stopped and the remaining water in the still boiled out and the fire pulled. When the boiling has subsided, the rosin valve or gate at the bottom of the still is opened and the hot rosin allowed to flow out. This rosin is passed through strainers, setting above a wooden vat. These strainers are made flat and consist of fine copper or brass wire above which is placed a layer of cotton batting. This batting retains the chips and fine bark that was present in the gum. The hot rosin drops through the strainer into the vat and when it is cool enough, it is dipped into barrels, drums or bags.

The original virgin gum when distilled should yield, if not exposed to the air too long, about 20 per cent of turpentine, 66½ per cent of rosin, 4½ per cent of chips and other extraneous matter, and about 9 per cent of water. A unit is considered to be 1 cask of turpentine (50 gals.) and 3⅓ bbls. of rosin (500 lbs.). The scrape gives about one-half as much turpentine as the gum.

There have been many changes in the foregoing operation. The gum as it is brought to the stills contains water, chips, pine straw and dirt. The presence of these impurities has a tendency to darken the rosin. At some stills the gum is placed in a separate vessel and heated above a screen, in which case the clear gum filters through the screen to the bottom, from which it is pumped to the still. At one place the gum is heated over brine and the dirt and chips settle to the bottom while the clear gum is decanted. In another case the clear gum is dissolved in turpentine to make it of a thinner consistency, so that the dirt and chips will fall to the bottom. A filter press is also recommended for filtering the hot gum or diluted gum.

Usually when the gum is cleaned before distilling, it is finished in a steam-heated still. Such a still has been designed by the Forest Service engineers and consists of a copper still, similar in shape to the fire still. It has a convex bottom and is supplied with a steam coil and a sparge for heating and distilling the turpentine. Vacuum stills have been tried as in foreign practice.

All such additions mean more original plant cost. A steam still requires a very much larger boiler than a fire still. A more recent innovation is the use of a special oil burner in the furnace of a fire still. This is further expense for equipment, but the equipment manufacturers claim that the savings justify the expenditures.

Gum turpentine is usually sold in wooden casks holding about 50 to 54 gallons. To keep them tight a coating of glue is placed on the inside. By rolling a cask about, containing 5 gals. of hot glue, and withdrawing the excess glue a coating of glue is left on the inside. After the coat dries a second coat is put on in a similar manner and when dry it is ready for use. As there is a little water left in the turpentine, unless this is removed by dehydration or complete settling, the glue is softened and the cask leaks. Because of this galvanized drums are being used in quantity.

Gum rosin was formerly placed in wooden barrels put together at the still. They were quite slack so it was necessary to lute the seams with clay. A shiplap barrel is now made which is much better. The tendency now is to use light galvanized steel drums. These store better and, being lighter, the freight per package is less.

The gum naval stores industry is now being subsidized by the Government. As a consequence of this, changes are being made in the selling practices that have held heretofore. Some of these changes are as follows:

Instead of bidding on an entire line consisting of all grades of rosin, each grade is purchased by itself on its own merits.

Rosin has been quoted on a basis of 280 lbs. gross in wood barrels and 230 lbs. net in steel barrels. Now it is bought by the 100 lbs. net weight, allowing 17 per cent tare for the wood barrels and actual weight of the drum as the tare for drums.

Turpentine has been quoted by the gallon in barrels. It is now quoted by the gallon in bulk. Formerly a gauge gallon was delivered at the temperature prevailing at the time of delivery. It is now sold by weight using 7.2 lbs. as the average weight per gallon. If sold on a seven-pound basis, allowance must be made in the price quoted.

A great deal of work has been done for the gum naval stores industry by the various agencies of the Government and complete information can be obtained concerning proper methods of manufacture and marketing from the proper agency, e.g., The Naval Stores Investigations Bureau of Chemistry and Soils, U. S. Department of Agriculture.

This brief treatise on Wood Distillation has shown that this industry has had a long history. It was important and prosperous during the earlier days before the bulk of our modern chemical industry was even visualized. Then it began to suffer serious reverses, first the loss of the major market for charcoal, then the competition of new materials, particularly synthetic methanol and acetic acid. Although it may never rise again to its one time prominence it now shows new life, as evidenced by the application of modern equipment and scientific methods. Particular emphasis is being placed on more efficient processing and more complete utilization of by-products. This adaptability gives assurance that wood distillation will remain a vigorous industry.

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CHAPTER 18

INDUSTRIAL CARBON, BLACKS, AND CHARS

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DESCRIPTION OF THE MATERIALS

Carbon in its elemental and allotropic forms, other than in its use as a fuel, is an essential of our modern civilization. Its value to industry is shown by the annual production of carbon and its related products to the extent of more than one hundred million dollars.

The various forms of carbon, such as industrial diamonds, graphite both natural and artificial, gas adsorbent chars, decolorizing carbon, metal adsorbent products, pharmaceutical chars, bone black, carbon pigments such as lampblack and carbon black as well as the miscellaneous black paint and ink pigments, manufactured carbon products such as electric furnace electrodes, electrical machinery brushes, specialties such as disks and telephone carbon, arc light electrodes, lead pencils, resistor carbon, refractories, carburizers for case hardening, crucibles, foundry facings, and other portions of the technology of carbon in industry, will be discussed in this chapter.

DIAMONDS

Diamonds are the hardest and most imperishable of minerals. The hardness of the diamond makes it indispensable for many abrasive purposes. Numerous efforts have been made to produce diamonds artificially but thus far without commercial success.

Physically the diamond has been the subject of much study. Its base, carbon, is chemically identical with graphite or charcoal, into which it can be resolved by the action of heat or electricity.

There are three well-defined varieties of diamonds, all finding industrial applications. They are the crystallized or gem variety; bort, also known as bortz, boort, boart, or bowr, a round form with radiate or confused crystalline structure; and carbonado, also known as black diamond carbon or carbonate, an impure aggregate of small diamond crystals which forms a rock, granular in texture, compact, and without cleavage. The definitions of gem and carbonado are followed by the trade, but the term bort is extended to all impure diamonds and even to fragments and powder of gem diamonds which, because of impurities or small size, are valueless as gems. A special variety of bort is known as ballas. It is round in form, light in color, and consists of crystals radiating from a common center. It is used as a test stone for determining the hardness of diamonds. Ballas is relatively rare, probably only a dozen or so of the bigger sizes being found per month on the average.

Fluctuations in the prices of gem and industrial diamonds are independent of each other. The value of carbonado is determined by the size and quality of the stone, the value per carat of a half-carat stone being about one half that of the carat stone and about one third that of a three-carat stone. The price of the material should increase, as the demand is increasing and no new carbonado areas are being found.

Carbonado—Carbonado is found in important quantities only in the states of Bahia and Minas Geraes, Brazil. Carbonado is opaque. It may be of black, dark green, brown, red, or gray color, generally, however, with a lustrous black surface. The stones range in size from a quarter of a carat to several hundred carats each. The large stones must be split by pressure into marketable shapes and sizes. Carbonado splitting requires expert skill.

The inner faces of freshly broken carbonado are light gray in color and resemble close-grained steel. When exposed, the broken surface gradually oxidizes and finally assumes a dark ash gray color. Carbonado, being a confused aggregate of very small crystals, has no planes of cleavage and is, therefore, less liable to fracture. It is stated that the best stones are those greenish black in color which show surfaces like fractured steel when split, and the greenish and reddish stones which show very small crystals. The reddish coloration is due to iron oxides.

Bort—Bort occurs in the Brazilian and British Guiana alluvial deposits and in the South African pipe and alluvial mines. The best grades are the Brazilian ballas, equal in value to the better grade of carbonado. They are very hard, globular stones found in small quantities, the yearly production being only a few hundred carats. Bort is distinguished by the diamond merchants as Cape Round borts, Cape ballas, Brazilian bort, and qualities bearing the names of mines producing them. Many of these borts are impure white, brown, black, or yellow diamonds that have less value for polishing than for industrial purposes. About one half of the South African pipe mine production is suitable only for industrial purposes, the alluvial mines producing relatively less poor material.

Diamonds, cut into various shapes, are set in lathe tools employed for a large number of purposes. Carbonado is most suited for this use, as it is less likely to fracture and is readily shaped. Bort, however, finds its largest use in this field because of its relative cheapness. The diamond-set tool is finding increased use in the truing of abrasive wheels. Eighty-five per cent of the stones employed for this purpose are bort with a small proportion of ballas, the rest being carbonado. Diamond-set tools are also used for cutting various hard substances such as hard rubber, ivory, electric light carbons, vulcanite, and to shape felt rolls in paper mills.

Diamond Dust—Diamond dust is a superior abrasive due to the rapidity with which it does its work. As its grain size is not rapidly reduced, it does even, dependable work, better than that of carborundum or other cheap abrasive. Probably the largest use of diamond dust is in the polishing of diamonds and gem stones.

Industrial Uses of Diamonds—Dies for wire drawing constitute one of the principal uses for industrial diamonds. The stones used are cleavage plates or thin crystals and ballas weighing from one half to ten carats. A hole, tapered at either end, is started in a thin fragment of diamond by a diamond point and finished by a steel drill fed with diamond dust. The drilled diamond plate is then mounted on a non-ferrous metal disk. When the aperture of a die has enlarged through use, it is redrilled to draw the next largest size of wire. The sizes of wire drawn vary in diameter from 0.114 inch (2.9 mm.) to 0.0008 inch (0.02 mm.), although holes as small as 0.0004 inch (0.01 mm.) have been used. In the drawing of fine wire, successively smaller dies are used, the usual practice employing diamond dies only in the final drawing. Tantalum, tungsten, and osmium filaments for electric lamps are drawn through diamond dies. Three hundred to four hundred tons of copper wire can be drawn through a single die without variation in gauge.

Diamond drilling is one of the important uses of carbonado. Some diamond dealers estimate that in boom mining times 7500 to 10,000 carats are used annually. The carbonado to be used in diamond drilling is broken up into fragments usually weighing up to three carats, although in certain cases weights as high as twenty carats may be used. The stones are then mounted in metallic drill heads. Carbonado to the value of $25,000 has been used in drilling single holes.

Diamonds, frequently of gem quality, varying in size from one eightieth to one fourth of a carat, are largely used in glass cutting. The diamond is set in a fusible metal at the end of the handle, and reset when the edges are dulled. Angular diamond crystals will cut the glass so that it breaks along the groove so produced. The edges and ends of rolled plate glass after it comes from the annealing kiln are trimmed with diamonds.

Diamond points set in drills find wide application in boring holes in watch jewels, optical instruments, and in drilling very hard substances with extreme accuracy of gauge. They are also used for making etching marks or engraving on scientific equipment, and in making intaglios.

GRAPHITE

Natural Graphite—Natural graphite was used in the Middle Ages as a drawing medium, and evidences of even earlier usage for decorative purposes have been found in prehistoric burial grounds in Europe. Its nature and identity as elemental carbon, however, were not established until the latter part of the eighteenth century, when Scheele, igniting it in a current of oxygen, demonstrated its carbon content.

Graphite is a black, lustrous mineral crystallizing in the hexagonal system with rhombohedral symmetry. The crystals have tabular form and are six sided, the faces commonly striated. They are seldom very distinct because of the softness of the material. Graphite is softer than talc, which is 1 on the Von Moh hardness scale, on which the diamond is 10.

The streak of graphite is black and lustrous. The mineral is easily sectile, flexible, but not elastic. Because of its softness it marks other substances readily and is greasy to the touch. It is a good conductor of heat and electricity. The flakes have a perfect basal cleavage and are opaque even in the thinnest scales. Graphite is highly resistant to weathering influences and to attack by most chemical reagents.

The natural graphites are divided into three classes, according to the character of the mineral. These comprise disseminated flake, amorphous or black lead, and crystalline or plumbago.

Flake Graphite—Flake graphite is a scaly or lamellar form commonly found in metamorphic rocks such as crystalline limestones, gneisses, and schists. In such cases, each flake is a separate individual and has crystallized as such in the rock. The extraction of flake graphite from its ores and its preparation for market have always presented difficulties from both the technical and the economic side. Fresh, unaltered flake ores, which are found in many Canadian deposits, range from 10 to 30 per cent graphite. Soft decomposed ores, such as from the Passau, Bavaria, mines, run from 30 to 50 per cent graphite. The minerals associated with flake form 75 to 95 per cent of the ore and possess specific properties varying little from those of graphite itself. Mica, of somewhat the same form, hardness, and toughness, behaves in much the same fashion as does graphite at all the stages of the mechanical treatment. It is one of the most difficult minerals to eliminate. Its presence in crucible graphite becomes highly objectionable, owing to its low fusion point.

The crucible trade, which uses about three quarters of the world's output of graphite, demands the best quality, pays the highest prices, and specifies No. 1 flake. This material must contain 90 per cent carbon or better, and be of such a screen size that all of it passes through a 20-mesh but is retained on a 90-mesh screen. Processes have been devised which have proved more or less satisfactory as far as carbon content and size of flake are concerned. These results, however, have always been achieved at the expense of recovery, and frequently by some system of retreatment that rendered operations unprofitable.

Graphite ores vary so widely in their character, proportion of large-size flake, nature of the associated minerals, hardness, and graphite content that it is quite impossible to outline any mill method that will even approximately suit a majority of ores.

Amorphous Graphite—Amorphous graphite is commonly found in the form of minute particles distributed more or less uniformly in feebly metamorphic rocks such as slates or shales, or in beds consisting almost entirely of graphite. The latter usually represent metamorphosed coal seams, carrying as high as 80 to 85 per cent graphitic carbon, while the former, being altered carbonaceous sediments, generally range from 25 to 60 per cent. The graphite content of such amorphous deposits depends upon the amount of carbon originally present in the sediments.

Due to the great variation in the carbon content and physical character of amorphous graphites, the treatment to be undergone is determined largely by the use to which the material can be put. Mexican graphite is of exceptionally high grade, being 86 per cent carbon. For this reason and because of its extreme softness, it is well adapted for pencils and lubricants. Rhode Island graphite is impure and somewhat hard. It is used almost exclusively for foundry facings. Other impure amorphous graphites with 35 to 50 per cent carbon can be utilized in paints, stove polishes, and for similar purposes. This ore is generally prepared by hand picking and grinding. For many purposes a high carbon content is not essential, and the presence of a considerable proportion of clayey matter is not objectionable.

Crystalline Graphites—The crystalline graphites are the purest of the natural graphites. As a result of their vein occurrence, the amount of mineral impurities, generally calcite and quartz, is small. The crude ore runs 60 to 70 per cent graphite. At the Ceylon mines where practically all the world's supply of plumbago is produced, the ore is first roughly picked over, the attached gangue reduced to 5 to 10 per cent, then shipped to the curing or dressing compounds on the coast. Here the larger pieces are picked out and the remainder sized by means of stationary inclined screens. The large pieces are broken up by hatchets and the impurities removed as far as possible by picking. The cleaned graphite is similarly sized. The larger pieces are placed on strips of wet sacking, again picked over, rubbed up by hand, and polished on a fine mesh screen placed flat on the ground. These larger sizes, which measure up to 1 inch across, are graded as "ordinary lump" and "medium lump." They command the highest prices. The graphite which passes through the screens is graded into "chip" and "dust," according to size.

The lower grade material is pulverized with wooden mauls or beaters, placed on sacking and sorted by hand. In some cases cleaning is done by washing in saucer-shaped baskets moved by hand, with a panning motion through water. The graphite is thrown off into the water, particles of gangue remaining in the basket. The cleaned graphite is shoveled up, dried by sun heat on drying floors, then winnowed into "dust" and "flying dust." The main grades—lump, chip, and dust—are further subdivided into several qualities, each one of which is a blending of the products of various mines.

Graphite or plumbago crucibles, made of a mixture of clay and graphite, are largely used in the melting of metals. The graphite contributes toward the refractoriness and heat conductivity of the mass, prevents oxidation, and produces a smooth surface for pouring. The function of the clay is that of a bonding material, which makes possible the forming of the crucible and the cementing of the graphite flakes. At the same time it covers them and prevents their oxidation.

Preparation of Graphite—The graphite is ground in burrstone mills or disintegrators and sized by screens. The sized material is proportioned with dry ground clay and mixed in a kneading machine. The mixed material is made just softly plastic by the addition of water, kneaded to a uniform consistency, and then set aside in a clay cellar to "age." Aged material is shaped by means of the potter's jolly in cloth-lined metal or plaster molds, then set aside to dry on the drying floor. Dried crucibles are fired in muffle kilns to a temperature a little above the dehydration point of the clay, i.e., 600° to 700° C. Graphite crucibles, like all other materials containing clay, are hydroscopic and should be freed from moisture by gently heating before being put into use. Disregard of this precaution causes the loss of thousands of crucibles annually.

Characteristics of Graphite Crucibles—The refractory quality of a crucible is much misunderstood. It is not so difficult to provide for refractory quality alone as for the other requisites of a good crucible. The range of refractoriness is very great. The crucible giving good service at the temperature of nickel fusion is not well adapted for service in spelter castings. The mixture must be varied according to the service required.

The graphite in the wall of the crucible begins to oxidize at about 600° C

The rate of oxidation increases with the temperature and varies with the composition of the furnace gases. The life of a crucible depends largely on the nonoxidation of the graphite. The glaze on the outer surface delays this oxidation, but the glaze is dependent on the refractoriness of the crucible mixture. Hence if the material be too infusible, the life of the crucible is very much shortened; but if it be too fusible, it softens and fails to protect the graphite. Some users coat the outside of the crucible with a mixture more fusible than the crucible wall itself. If the first heat to which a crucible is subjected be high enough to produce this protective glaze, its life at lower subsequent heats is much prolonged.

The various kinds of work in which graphite crucibles are used as the melting vessel include malleable castings, small iron castings, crucible cast steel, all kinds of copper and zinc alloys, spelter castings, file tempering, and precious metal melting and refining. Oblong, square, and round shapes are used in liquid brazing and as calcining trays or boxes for material requiring careful even heating without exposure, such as pencil leads, incandescent carbon filaments, and so forth.

Other graphite refractory products used in foundry work and in metal smelting are made from mixtures of graphite and refractory clays. These articles include crucible covers, stopper heads for open-hearth steel ladles, pouring nozzles, stirrers, rings, jackets, skimmers, dippers, phosphorizers, crucible extension tops, pyrometer shields, and miscellaneous furnace articles.

Many special forms of crucibles are used in industry. The tempering crucibles for files and tool steel are usually cylinders, the manufacture of which is conducted in the same manner as that of graphite crucibles. The tempering crucibles are filled with either molten lead or hardening salts. The heated steel from the forge is immersed in these tempering baths so as to effect a gradual cooling.

Brazing crucibles are of many different forms and shapes, usually having straight sides sloping in a "V" shape toward the bottom. Extension tops or funnels are used on top of crucibles to allow the addition of a larger charge of turnings or chips of metal. This reduces the necessity of frequent additions of small quantities.

Pyrometer shields are usually closed end cylinders made entirely of graphite without a clay bond. These serve as protections for the wires of thermo-electric pyrometers. Graphite crucibles used in pyrometer calibration are ordinarily cut or machined out of solid pieces of artificial graphite. Pyrometer shields are usually made in the same manner, also from artificial graphite.

Lubricating graphite becomes possible because the very low coefficient of friction of graphite is retained under practically all working conditions. It is soft and readily adheres to metallic surfaces even under light pressures. Its property of filling the pores of a metal makes it very valuable for lubricating work. The surfaces of bearings lubricated with graphite become covered with a veneer of the material, which reduces the bearing coefficient of friction to practically that of graphite itself. Graphite is remarkably resistant to most chemical action. The veneer it forms on bearing surfaces tends to protect them from the action of corrosive solutions or vapors. This is particularly true in the case of cylinder lubrication where high-pressure steam, oil, or gas is used. Oil and grease lubricants under these conditions tend to lose body or to char or vaporize under the action of the heat and gases to which they are exposed. In heavy bearings, oils and greases show a tendency to squeeze out from between surfaces. The metal parts then come in contact, with resultant wear. Graphite, forming a coating on both metal surfaces, allows a graphite instead of a metal contact to be secured.

For ordinary lubrication in open bearings, slides, gears, and similar places, the graphite is usually mixed with oil or grease. A great variety of such compounds is found on the market, each claiming unusual and specific properties. Many of them are designed for work under special conditions such as exposure to salt water, acids, or alkalies, in dredges, winches, and mining machinery, or at different temperatures where varying degrees of viscosity are required.

Miscellaneous Uses—Foundry facings in general are the sands which form a layer about an inch thick around a pattern. In the specific sense of the term, they refer to those materials used to give the insides of the molds a smooth finish, so that the castings part freely and cleanly on cooling. Graphite is the most important material for this purpose. The consumption in foundry facings is greater than in any other field, with the exception of crucible manufacture. The low-grade dust graphite from the refining mills, running about 40 to 70 per cent carbon, finds practically its only outlet in these facings. Many foundry facings on the market run 60 to 70 per cent carbon, but a considerable percentage of this is non-graphitic.

Graphite itself possesses no adhesive properties. Refractory clays are therefore added as bonding agents. The binder absorbs a certain amount of moisture from the mold, thus holding the facing in place. When the clay is calcined by the molten metal, the facing is rendered somewhat porous, thus allowing moisture and occluded gases to escape. Proper proportion of the graphite and the binder is important, since if there be too much of the latter, stripping becomes difficult, and if too little, the graphite runs before the metal or floats on it.

There are a number of miscellaneous uses of graphite of importance, although they consume small tonnages. Among them we find its employment in electrotyping, stove polishes, boiler graphite, powder manufacture, and in various industrial applications.

Very finely powdered graphite is used for two purposes in electrotyping. The forms, completely made up, are dusted over with graphite, placed in the machine, and highly polished. This allows clean, sharp stripping of the type from the wax mold. In its second use, the wax mold, bearing the impression of the original, is dusted with graphite which spreads freely over the whole surface and into the fine crevices of the mold. The wax form is then polished and is ready for immersion in the electroplating bath.

Amorphous natural graphites are generally used in stove polishes. They are worked up into the form of a paste, a cream, a powder, cake, or liquid with the addition of a clay, resin, asphaltum, or soap binder in the case of the solid polishes, and of a gasoline or water vehicle for the liquid varieties.

The use of graphite for the prevention of scale in boilers has often been advocated. Its action is purely mechanical. It is not affected in any degree by the alkalinity or acidity of the boiler feed water, or by the temperature. Small particles of graphite work their way through the cracks in old scale, penetrating between the scale and the metal. The former is thus loosened so that it may be easily removed. If the use of graphite be adopted when a boiler is first put into operation, any great accumulation of hard scale may be effectively prevented.

The particles become incorporated with the scale as it forms, making it soft and friable.

Graphite is used in engine packing, hard rubber compositions, cord and twine manufacture, hat polishing, and in the manufacture of cordage, ropes, and cables. It also finds application in various types of washers and packing, particularly for piston type machines. Mixed with lead it forms one of the most suitable high-pressure corrosion-resistant packings we have.

Artificial Graphite—Artificial graphite is discussed under electrochemical industries in Chapter 12, which see. It is ordinarily much purer than the natural graphites. Its various special forms such as electrodes, brushes, contacts and other shapes are discussed under these specific headings.

CARBON BLACK

Carbon black (also known as gas black, natural gas black, ebony black, jet black, hydrocarbon black, satin gloss black, and silicate of carbon) is the material resulting from the incomplete combustion of a gas, deposited by actual contact of a flame on a metallic surface. It was first manufactured from artificial gas. The product is very glossy, has an intense color, and makes a high-priced printing ink. Carbon black of slightly lower grade made from cheaper natural gas is the commercial product on the market today. It is a fluffy, velvety black material of very great fineness.

Carbon black is produced by one of the following methods: (1) formation by direct contact of a flame upon a depositing surface, usually of metal; (2) production by heating carbonaceous vapors or gases to a decomposition temperature by external heating with or without air in the forming chamber. The latter method is generally termed cracking or thermal decomposition. It produces a soft black not unlike lampblack, sometimes grayish and semi-graphitic.

There are five processes of manufacturing carbon black from natural gas. They are the channel system, the small rotating disk, the roller or rotating cylinder, and the large plate process. These methods differ chiefly in the size and shape of the surface upon which the black is collected and in the rate of travel of the moving device. Fully 80 per cent of the product manufactured today is made by the channel process. Classified according to the quantity of carbon black produced, the order becomes: (1) the channel, (2) the thermatomic, (3) the small rotating disk, (4) the large plate, and (5) the roller process.

In the channel process the black is deposited on the smooth undersurface of structural steel channels by lava tip burners. The channel irons are usually built in tables of eight, sometimes 100 feet long. They are given a slow reciprocating motion that scrapes the deposited black into hoppers. From here it is carried by screw-conveyors to the packing house where it is bolted and packed. The mechanism is enclosed in sheet-iron buildings so that the amount of air may be regulated. Variations of the amount of air, the speed of scraping, and the pressure of the gas control the quality of the product.

The cracking process or thermal decomposition is carried out in a furnace, similar to a blast furnace, filled with checkerbrick. The furnace is heated to the desired temperature, the heating gas and air turned off, and the natural gas to be cracked introduced. The process is generally an intermittent one. The resultant black leaves the furnace in suspension in the residual gas, which is cooled by water sprays. The carbon black is then filtered from this gas through fabric bags, sent on by conveyors to the bagging house, where it is packed. From 6 to 10 pounds of carbon per thousand cubic feet of natural gas used are recovered.

In the small rotating disk process, the depositing surface is a cast-iron disk from 3 to 3½ feet in diameter, the gas being burned through a burner ring underneath the disk. The carbon black is scraped off continuously.

The plate or Cabot process employs stationary plates 24 feet in diameter for depositing surfaces. Revolving scrapers and burners are located underneath the plates.

In the roller process the gas burners are located directly underneath the rotating cylinder which is the depositing surface. At the present time roller process black is the highest grade of carbon black. It is used chiefly in making lithographic and embossing inks and printing inks for half-tone engravings.

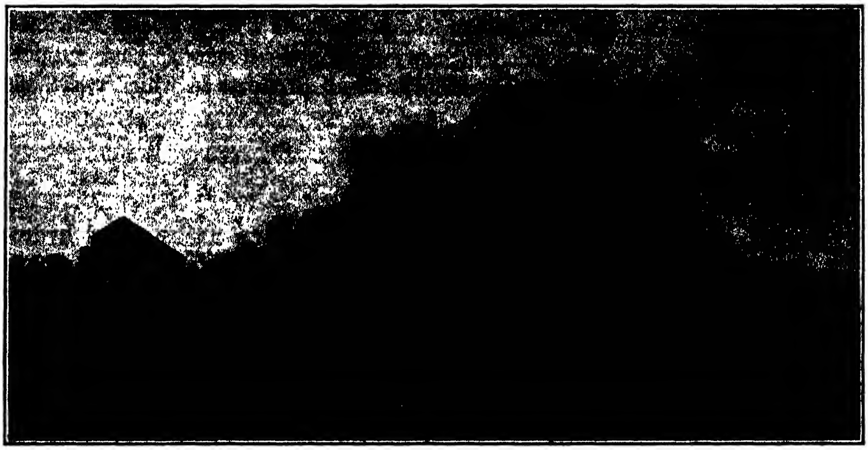

FIG. 1. A Louisiana Carbon Black Plant in Operation.

Uses of Carbon Black—Given in the order of importance, the uses of carbon black are in the manufacture of rubber, printing ink, paints and enamels, lacquers, stove polishes, other products such as phonograph records, carbon paper, crayons, typewriter ribbons, black and gray paper, tarpaulins, black leather, bookbinders' board, marking and stenciling inks, rubber goods, artificial stone and black tile, insulating materials, electric arc carbons, buffing powders, and to a very small extent in case hardening. From 200 to 300 million pounds per year are used in rubber, 20 to 25 million in printing inks, approximately 10 million pounds in paints, about 4 million pounds in stove polishes, and somewhat more than 10 million pounds for other miscellaneous uses, not including more than a hundred million pounds annually exported.

For certain purposes, such as phonograph records, medical hard rubber, all soft rubber goods like footwear, tubing, and heavy truck tires, certain kinds of printer's ink and black paint, it is possible to substitute lampblack for carbon black. For most purposes, however, these two products are quite dissimilar in their physical properties and to date have proved unsuitable for substitution.

Carbon black finds its chief use in rubber because its finely divided state greatly reduces oxidation and increases the tensile strength of the mixture. It is not considered as indispensable in rubber as in printing inks. In times of high prices, carbon black has often been supplanted by zinc oxide or graphite. Zinc oxide, an important filler, became too costly soon after the outbreak of the First World War. It was then shown that carbon black could be successfully used as a substitute.

Carbon black as a rubber filler is now used to the extent of 3 to 55 per cent, according to the purpose for which the rubber is required. On a volume basis, carbon black with a specific gravity of 1.8 costs only one third of zinc oxide with the specific gravity of 5.6. In actual practice, however, a greater volume of carbon black is used than of zinc oxide, so that the resultant mix contains less rubber per unit volume than the zinc oxide mix.

The use of carbon black in rubber compositions is by no means restricted to automobile tires, but has spread to many other articles such as hose, surgical and mechanical rubber, floor compositions, and all products in which resistance to wear is a prime requisite.

LAMPBLACK

Lampblack is, generally speaking, the smoke from an unobstructed hydrocarbon flame, the solid particles being deposited in chambers as the smoke is conducted through flues from the furnace. Various oils, fats, and resins have been used for centuries to make lampblack, the resins to a greater extent than other materials. They were generally heated in an iron pan over a small fire, ignited, and the smoke led into tents lined with sheepskin. The sides of the tent were beaten at frequent intervals to knock down the deposit of soot.

In Continental Europe where natural gas is not available, lampblack is employed for many of the purposes which, in America, are entirely met by carbon black. Lampblack is of a very soft, flocculent nature, whereas carbon black is hard and brilliant. The "tinting strength" of carbon black is many times that of lampblack.

The most primitive method of making a soot pigment like lampblack consisted in burning materials like resins in a closed room. The material burned until stifled by its own smoke through lack of oxygen. No doubt the principle of restricted air supply was adopted in ignorance. The method was slow and costly, yielding small amounts of a poor material. Much unconsumed material such as empyreumatic bodies, oils, and heavy bad-smelling substances remained in the black.

Many changes have been made in the furnaces and chambers for the manufacture of lampblack, but the principle remains the same. A modern plant consists of one or more furnaces burning oil with incomplete combustion. The proper amount of air is admitted through the regulation of suction and blower fans.

It was not until coal tar oils (or, specifically, those designated in the trade as "dead" or creosote oils) were commercially available that there was any distinct improvement in the method of making lampblack. It was not practical to melt materials such as resins and naphthalene to make them flow readily through pipes, nor to burn them in pans so that impurities and free oil might not be carried over into the black. By the use of tar oils, however, different methods were possible.

The buildings now used for this purpose, both in Europe and in the United States, consist of a brick or stone structure with a number of specially constructed furnaces at one end. These furnaces are connected by large pipes or openings into a series of condensing chambers communicating one with the other. Air is admitted into the furnace through vents in the form of registers which can be regulated during the process of burning the oil.

In the United States both tar oils and petroleum oils are used. The oil is conducted through pipes leading into the furnaces, each furnace having a separate supply pipe. The oil passing through these pipes drops upon pans or plates heated to a temperature sufficient to ignite the oil. The smoke is liberated from the flame, passing through the openings into the condensing chamber, where the black is deposited.

Generally speaking, the best grades of lampblack are obtained in furnaces of moderate size so built that the black is practically calcined at the time it is deposited. It will then carry down little empyreumatic matter. The products of combustion are usually carried through a series of chambers where baffles or partition walls force the gas streams to deposit lampblack. Proper baffling may increase the percentage of decomposition of the raw material being burnt. Poorly designed baffles or too great a number will enforce a high rate of gas velocity in order to force the products of combustion through the system. In this way lampblack particles may be carried along in the gas stream and not deposited.

There are many grades of lampblack—more than of its sister black, carbon black. Some of it is shipped in sugar barrels packed full, containing only five pounds. The same barrel will hold 100 pounds of another grade. Chemically the two materials may be practically the same, but physically they are very different. This is due entirely to the amount of occluded gases and the particular shape of the particle. Lampblack particles are somewhat like elongated tadpoles. They flock together in the manner of floating cobwebs.

Lampblack has been used for printer's ink ever since the invention of the printing press. After the advent of carbon black in 1864, lampblack was employed less and less for ink making. Today it is little used except to impart certain properties to an ink already containing carbon black. Lampblack is used in the manufacture of inks, lead pencils, electrical machinery brushes, paints, metal polishes, stove polish, phonograph records, carbon paper, crayons, and black-colored materials as a filler.

Its specific gravity is less than 2. One pound of the material will occupy 200 to 230 cubic inches. It ordinarily contains 99 per cent or more of carbon. In certain applications, lampblack is considered superior to carbon black as a paint pigment in some gray tints, because of the bluish gray tones of lampblack. It was formerly known under the name of gloss soot, light soot, flame soot, and flame black.

MISCELLANEOUS BLACKS

The miscellaneous blacks, or rather the materials of carbonaceous nature which are known to the trade as carbons, such as gas retort coke, oil retort coke, graphite, carbon black, wood pulp black, willow charcoal, Frankfort and vine blacks, bone black, ivory black, sugar house black, and blacks made from refuse materials like the various organic scrap products, do not all possess the same flocculent characteristics, strength of color, chemical composition, or physical structure. Each black has its own specific uses and as a rule cannot be substituted for another. It is difficult to determine which black to use by means of ordinary tests, since the properties are sometimes altered in combining with other substances.

There is a characteristic difference between the smoke of a burning product and the charcoal or coke of the same product. All carbonaceous materials give up their volatile matter when burnt with an insufficient supply of air in a closed retort. The residue after distillation is charcoal or coke.

Acetylene Black—Acetylene black is produced from acetylene gas by thermatomic cracking, with hydrogen as a by-product, as well as by methods similar to that employed for natural gas.

Benzol Black—Benzol black is a soft non-granular black made from benzol in a manner similar to that in which carbon black is made from natural gas. It will remain in suspension in oil and varnish longer than carbon black. It is, however, regarded as a poor drier.

Drop Black—Drop black is a pigment made from bone black which is of no further use to the sugar manufacturer in removing the color from his product. The "spent" bone char is thoroughly washed and ground in burrstone mills to reduce the spongy carbonaceous matter to a fine silky powder. The old custom was to sell this black in lumps made by dropping the black paste, as it came from the grind mill, in little heaps on boards for drying. The production of black in peculiarly shaped pieces, according to this prescribed ritual, was a criterion of purity. The name "drop black" as used by the trade also applies to finely powdered bone black. It contains 10 to 20 per cent carbon and 80 to 90 per cent calcium phosphate.

Ivory Black—Ivory black or "extract of ivory black" was formerly made from charred ivory chips which had been digested in hydrochloric acid to dissolve out their calcium phosphate content. It possesses intense black staining power. The present-day ivory blacks are forms of bone black.

Mineral Black—Mineral black is a black pigment made by grinding to a very fine degree a clay shale or slate containing about 30 per cent carbon. When properly ground and washed, it is a fine soft powder. It is often used in making mixed blacks for plate printing inks, as well as for a cheap paint filler and pigment.

Special Black—Special blacks, used principally for adding to other materials, are made from coke, lignite, and certain by-products. One of them is blood black, a very soft material made by charring blood. It has a strong adsorbing power for alkaloids and coloring matters. Another is leather black, made from waste and scrap leather. The ash, carbon content, and properties of the special blacks vary with the raw material.

Swedish Black—Swedish black is a pigment which is in effect a modified lampblack. It is made by carbonizing the bark of the silver birch tree packed in retorts. The resultant material is a mixture of charcoal and lampblack. It finds miscellaneous applications as a pigment.

Vine Black—Vine black refers to those pigments produced by the dry distillation and carbonization of willow wood, wine yeast, grape husks, grapevine twigs, spent tan bark, shells, fruit pits, sawdust, or in fact any material of vegetable origin. The carbonaceous residues from grapevines and similar materials are also known as Frankfort black. Many of these products today are made from wood pulp black, a paper manufacture by-product.

PRINTING INKS

Printing inks from the earliest known times were made from carbonaceous material such as lampblack or related forms. The pigments, ground and mixed in boiled drying oils such as linseed, perilla, or similar substance, are incorporated with driers and various other constituents like varnishes, mineral oils, gums, etc., depending upon the specific qualities desired and the use for which the ink is intended.

The three main classes of printing are typographic printing, lithographic presswork, and depressed surface, plate or engraving impression. Modern rotary presses require a rapidly drying ink, free flowing to permit high speed operation. At the same time the ink must have high hiding and covering power, and make legible impressions instantaneously. Carbon black satisfies all these requirements. Nine pounds of ink containing one pound of carbon black and eight pounds of oil and other materials will print ninety copies of a three hundred page octavo book.

The black pigments which are carbon, with the exception of magnetic pigment and manganese black, are the most important ink pigments from the viewpoint of quantity consumed and breadth of application. They are practically all good, different ones being adapted to different classes or processes of printing. Some of them are of value as additions to certain inks to improve their working qualities.

The Various Ink Pigments—There are five classes of ink pigments: (1) bone black, (2) vine black or vegetable black, (3) carbon black, (4) lampblack, and (5) miscellaneous blacks.

Acid-treated bone black has a deep black color due to its fineness. It is of great importance as a toner for slightly off color or weak bone blacks and as a forcing black to bring up the color in certain classes of plate work. Its application is entirely restricted to plate printing inks. Vine blacks have a darker greenish-black hue than bone black. Their fairly low oil absorption makes a somewhat long ink with moderate flow. They are quite abrasive and do not make up into smooth inks. They are used as toners in plate inks.

Carbon black has great tinting powers and makes excellent typographical ink of fine working quality. The different brands and grades show a wide range of behavior in application, some producing short tacky inks, others making inks of great natural length and decided flow. Some carbon blacks, however, are worthless even for the cheapest news inks. Certain blacks exhibit great differences in their behavior toward driers, although the reason for this variation is not known. By a proper combination of varnishes and grades of carbon black, almost any desired effect in typographical printing ink can be secured. Good grades of carbon black have a deep black top hue and a brownish-black under hue. The material has a high oil absorption, due to the fineness of the particles. It usually makes a short, poor-flowing ink which is remarkably fast to light and resistant to atmospheric influences. Good grades of carbon black show no drying action. They are not abrasive and work up to a very smooth ink. Carbon black is the most important typographic black, being the basis of practically all black typographic inks today.

Lampblack has a deep black top hue and a brownish-black under hue. Like carbon black, it has a high oil absorption but makes a short ink with poor flow. Many of its properties are similar to the cheaper carbon blacks which have displaced it, but it does not give inks of the best consistency and is too gray in color.

Miscellaneous carbonaceous blacks used in printing are mineral black and mixed blacks. They are sometimes used for making very cheap blacks for printing ink. Mixed blacks have properties which are dependent upon the properties of their constituents. In many respects they are analogous to lampblack.

BLACK PIGMENTS

Black pigments find extensive use in various branches of the paint industry. The most important black paint pigments, given in the order of volume used, are carbon black, lampblack, and graphite. Other blacks such as the Frankfort blacks, bone black, ivory black, and mineral black are used to a much smaller extent. In the order of their importance, the chief physical properties to be looked for are color, tinting strength, fineness, oil absorption, specific gravity.

The term color refers to the relative blackness of a material when mixed with oil. It is only comparative.

The tinting strength of a pigment is its most important property from the paint manufacturer's standpoint. As applied to blacks, it is a measure of their ability to impart a gray hue to a definite weight of a standard white pigment.

The hiding power of a pigment is inversely proportional to the diameter of the particles. The finer the particles of a given pigment are when mixed to form a paint, the greater is its covering power.

Gardner[1] has given figures showing the percentage of oil required to grind pigments into average paste form: carbon black 82 per cent, lampblack 72 per cent, drop (bone) black 60 per cent, bone black 40 per cent, graphite (pure) 40 per cent. For contrast one may cite white lead (sublimed) 10 per cent, blanc fixe 30 per cent, barytes (natural) 9 per cent, terra alba (gypsum) 22 per cent.

For tinting and staining purposes either lampblack or carbon black is generally used. All blacks do not possess the same strength of color or tinting power. Carbon black has a much greater tinting strength than lampblack. Although the tinting strengths of various commercial grades of carbon black show great variations, approximately five times as much lampblack is required to do the same tinting work that one part of carbon black will do. Certain of the best grades of carbon black may have as high as ten times the tinting strength of mineral blacks.

Carbon black is acknowledged superior for varnishes and enamels. Its use is required in enamels in various black and gray paints supplied to the United States War Department. According to Toch[2] lampblack is superior to carbon black as a pigment. It is no doubt true that in certain gray tints lampblack is to be pre-

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[1] "Paint Technology and Tests," McGraw-Hill Book Co., New York (1911).

[2] "Chemistry and Technology of Paints," D. Van Nostrand Co., New York (1925).

tral and loses its metal adsorbing power, becoming an ordinary decolorizing char.

The technical problems involved in the adaptation of charcoal for the removal of gold and silver from cyanide liquors seem to have been met successfully in hydrometallurgical plants in Australia. Lump charcoal is unsuitable for this use because of the low efficiency and bulk of the material to be smelted. The practice involves wet grinding of the char, the resultant material forming a cake on the leaves of a leaf filter. The liquor to be treated is passed through several units in succession, the strongest liquor meeting the partly loaded char and the weakest liquors the fresh char. The cakes are dropped at intervals and reformed, exposing fresh surfaces and definitely increasing the capacity of the char. After washing and drying, the cakes are burned to remove the carbon. The ash is then collected and smelted with a special flux.

Pharmaceutical Charcoals—Pharmaceutical charcoals for use in medicine and pharmacy have shown a rapid development in recent years. Many of the commercial synthetic vegetable carbons find application, in small tonnages to be sure, in the manufacture of various types of pills, digestive tablets, and the like. The adsorbent action of charcoal for alkaloids, pathogenic bacteria, enzymes, toxins, and poisons of various sorts is well known.

OTHER USES OF CARBON

Carbon Electrodes—Carbon electrodes were first successfully manufactured on a commercial scale in 1876 by Carré, a Frenchman. At that time most of the work was in the direction of arc light carbons. The development of our present gigantic electric furnace electrodes[9] has taken place during the past two decades. The growth of the industry has been tremendous, turning out products to the value of about $11,000 in 1899 and over $12,000,000 in 1928, an increase of about a thousandfold in little less than three decades.

In 1878 Brush was making electrodes in the United States on a commercial scale from petroleum coke, then a waste product of petroleum refining that the oil companies burned under their stills.

Electrode production divides itself into five divisions: (1) the selection of the raw materials, (2) calcination of these materials, (3) grinding, mixing with a binder, and shaping, (4) baking the green shape, and (5) finishing, machining, and testing the final electrode.

Raw Materials. Almost all carbonaceous matters have at one time or another been used as starting substances, but today only two are used: anthracite coal, mostly for large electrodes for electric furnaces, and petroleum coke for reduction electrodes (e.g., for aluminum). Petroleum coke is the final residue of the intermittent distillation of petroleum. It is a hard, brittle substance of shiny, oily appearance, very high fixed carbon, and low in ash. It is one of the purest forms of carbon available in large quantities. Formerly it was a waste by-product; today, due to the electrode industry, the refiners regard it as a valuable commercial material. Only selected low ash coals, of low volatile content, are used as raw materials.

Calcination. The materials are freed of their volatile matter by heating to a white heat. The calciners employed are either developments of the industry and

[9] See also Chapter 12.

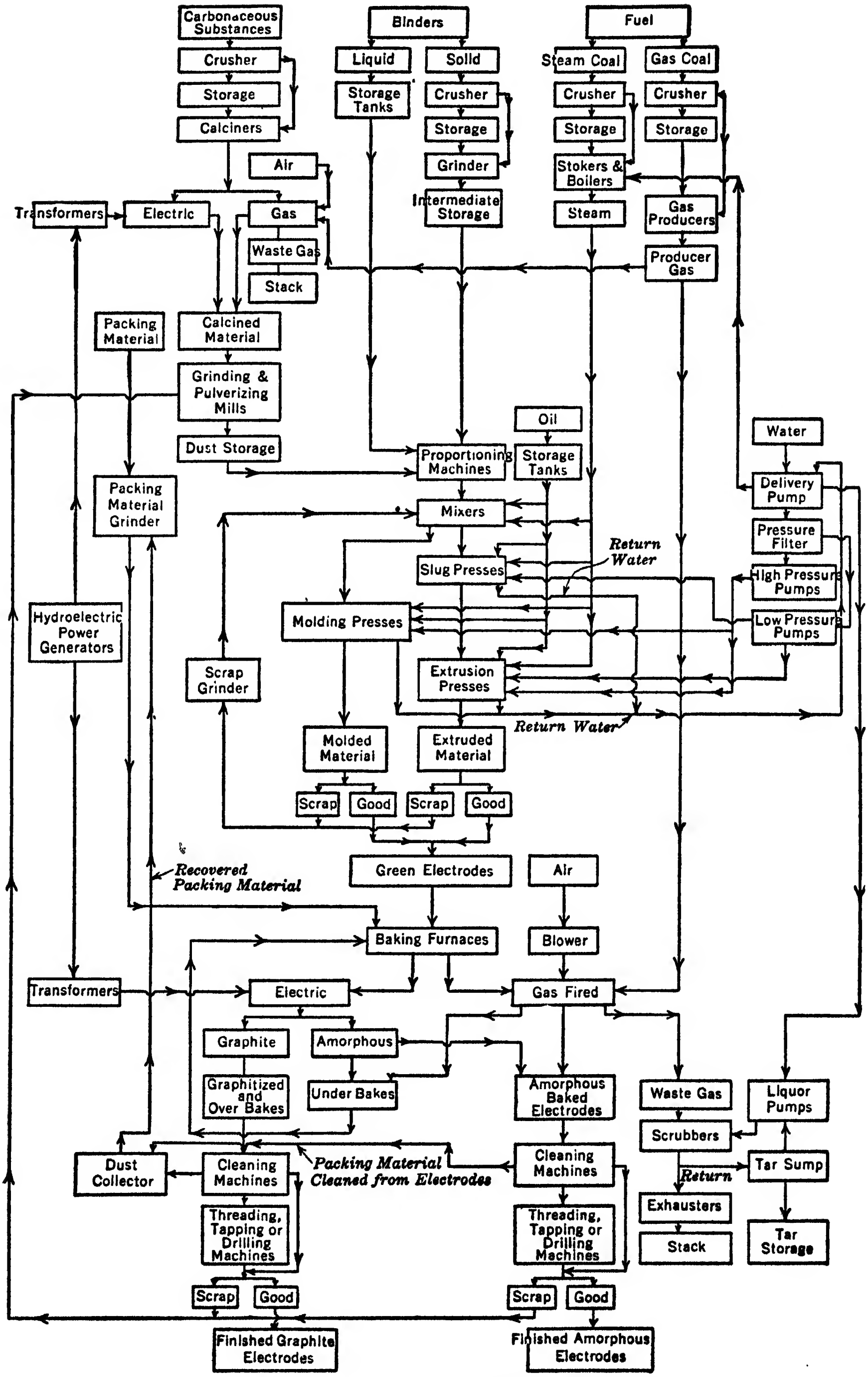

FIG. 6. Flow Sheet of Carbon Electrode Manufacture.

its close connection with electrothermic and electrolytic processes, or are adaptations from gas manufacture. The electrical types are commonly vertical, heating to the required temperature by the resistance of the charge to the electric current. The gas types are those of the Woodall-Duckam and Glover West vertical retorts.[10]

Grinding. The pulverization of the calcined cokes to a fine powder is done almost entirely in machines of the impact pulverizer or tube mill type.

TABLE 3—COMPARISON OF AMORPHOUS AND GRAPHITIC CARBON ELECTRODES

	Acheson Graphite Electrodes	*Amorphous Carbon Electrode* *	*Gas-Baked Amorphous Carbon Electrode* †	*Large Electro-thermal Electrodes*
Specific resistance (ohms per inch cube)	0.00032	0.00124	0.00161	0.00220
Specific resistance (ohms per centimeter cube)	0.000813	0.00325	0.00400	0.00550
Comparative section area for same voltage drop	1	3.8	4.4	6.8
Weight, pounds per cubic inch	0.0574	0.0564	0.0560	0.058
Weight, pounds per cubic foot	99.0	97.5	97.0	100.0
Apparent density, grams per cubic centimeter	1.585	1.558	1.55	1.60
Tensile strength, pounds per square inch:				
Lengthwise	800–1000	1000–1500	1000–1500	....
Crosswise	500– 600	600– 900	600– 900	....
Temperature of oxidation in air, degrees Centigrade	640	500	500	500

* Very good electric baked electrode (small). † Typical small electrode.

Mixing. The dust is proportioned from the storage bin with the proper percentage of binder, and delivered to the mixing machines. The binders are coal tar or pitch. Mixers are of various types, the one most commonly used consisting essentially of a steam-heated drum mounted on its side. Mixing is accomplished by the rotation of the central shaft with arms attached. The forward tilt of the arms, which during rotation carry the mix forward, finally discharges it through the door at the end of the drum.

Shaping. The material is shaped by compressing the hot plastic mass from the mixers either in molding presses, in steel molds so formed as to give the desired dimensions, or in slug presses where the mass is pressed together preparatory to the plug presses, through the orifices of which it is extruded in the shape desired. All shaping presses are operated hydraulically.

Baking. The shaped or "green" electrodes, of high electrical resistance and low tensile strength, are converted to a condition where their properties vary little with temperature, of low resistance and high tensile strength, by the process of baking in which the temperature is raised to approximately 1100° C. This temperature is high enough to carbonize the binder and, after carbonization, free

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[10] See Chapter 15.

it from all volatile matter. The furnaces used are either of the electric resistance type or of the gas-fired variety, adapted to the industry from those used in pottery manufacture. As the electrodes soften during baking, they are held in place by filling the interstices with finely ground petroleum coke, termed packing material. Some of the gas-fired furnaces are tremendous in size, sufficient to hold millions of pounds of electrodes and an equal amount of packing.

Finishing. After baking, the cooled electrodes are removed from the furnace and cleaned of all adhering packing material. They are tested for ash, resistivity, apparent density, volatile matter, and tensile strength. All rejected material, whenever possible, is sent back into process to be used as calcined coke. When desirable, the baked electrodes are machined for particular uses such as continuous feeding in furnaces. Table 3 gives some of the characteristics of good modern electrodes. The composite flow sheet shown in Figure 6 is self-explanatory. The manufacture of graphite electrodes is a branch of this industry.

The essential rôle of the carbon electrode in industry is attested by the fact that it enters into the manufacture of the following substances: electric steel, ferro-alloys, calcium carbide, silicon carbide and related abrasives, aluminum, calcium and magnesium metals, phosphorus and phosphoric acid, electrical resistance wire, titanium and zirconium, carbon disulfide, tungsten, cyanamid, sodium, caustic, chlorine, and the electric furnace alloys and products.[11]

Carbon Brushes—Carbon brushes for electrical machinery are closely related to electrodes in their manufacture. The processes are much the same, but due to the desirability of producing a low-resistance brush, only pure substances with as low an ash content as possible are used. A greater variety of raw materials may be used for brushes than for electrodes, due to the different characteristics and the wide range of products. The principal raw material, however, is the same, being petroleum coke, the purest industrial form of carbon available in large quantities. Other raw materials are lampblack, carbon black (on rare occasions some of the other blacks may be used in small quantities), and in some instances retort or gas carbon. Being a hard, dense material, retort carbon is sometimes used to give a cutting grain to the brush so that it will have a slight abrasive action. Metallic powders such as copper, zinc, lead, and tin, either singly or together, are employed in the so-called metal carbon or metal graphite brushes. Graphite is also an important raw material for brush manufacture, the natural variety in the form of natural flake, Ceylon plumbago, or Sonora (Mexico) amorphous being employed to a greater extent than the Acheson or artificial type.

The electrographitic brush represents the highest stage of manufacture. This type is made of carefully selected forms of amorphous carbon to give the desired characteristics of the finished product. Temperatures and time of exposure are regulated in the final baking, so as to graphitize all or part of the amorphous carbon. When entirely graphitized, the brush is as nearly absolutely non-abrasive as it is possible to be made.

The grading and selecting of materials in brush making to produce the specific qualities of brushes well suited for the varied electrical machinery of the present day have been brought to a high standard of perfection through the great amount of experimental work done by the various manufacturing companies. The amount

[11] For a discussion of these manufactures see Chapters 12 and 24.

of machine work on brushes is greater than on electrodes. Other methods of manufacture of carbon brushes involve grinding and calcining the raw materials and bonding the powders together with resinous substances, particularly of the heat hardening or thermally reactive type.

Arc Light Carbons—Arc light carbons are practically electrodes manufactured on a small scale. The raw materials are the same with the exception that retort carbon, lampblack, and graphite are often incorporated for specific purposes. Modern practice in arc light carbon manufacture is to add some metallic salts or oxides to the mix before extrusion of the green material, as these oxides increase the brilliancy of the light given off by the arc. The materials used for the production of white light are titanium, thorium and cerium oxides, monazite sand, ilmenite, lime, ferrotitanium, various metallic oxides and related materials. The United States patent literature gives a large variety of substances for this purpose. The binder is generally silicate of soda, although dextrines, caseins, water-soluble gums, and at times milk of lime as well as clays have been employed.

Battery Carbons—Battery carbons are small-size electrodes. They are made by both the molding and extrusion processes. In portable or small-size dry cells of the Leclanché type, they form one of the poles of the cell. Since they are not affected by oxidation as are furnace electrodes, the matter of obtaining high apparent density in their manufacture is not so important.

Carbon Specialties—Carbon specialties are articles of carbon molded in special shapes to predetermined characteristics or machined out of standard shapes to supply a specified demand. The non-fusing characteristics of carbon are of importance in the carbon and graphite contacts used on electric elevator controllers, automatic motor starting equipment, high amperage circuit breakers and the like, where a non-burning material is essential to long life of the contact. Carbon is most suitable for this purpose because of its electrical conductivity and its ability to withstand the action of the electric arc. Contacts are made of carbon or graphite, depending upon the carrying capacity required. The products, made by molding or grinding and machining, are turned out in a variety of shapes and sizes to conform to the demands of different electrical designs. In general, their properties are quite similar to those of brushes.

Telephone carbon is a crushed product made of carefully selected coals calcined to determined resistivity, vacuum treated, ground, and sifted to 60 to 80 meshes to the inch in its use for ordinary telephones, and 60 to 120 mesh for some special purposes. It must be hard material. The shape of the particles is of considerable importance. The characteristics of the finished product are carefully regulated by intensive control of all manufacturing operations.

Lead Pencils—Lead pencils, as far as their writing elements are concerned, are composed of graphite, wax, silica, and silicates often in the form of clay, together with lampblack and sometimes retort carbon or coal in small quantities. Softer pencils have greater percentages of graphite and wax (the binder), the harder ones greater percentages of clay and silica with correspondingly smaller percentages of graphite and wax.

Carbon Refractories—Carbon refractories are the only commercial refractories[12] which will resist very high temperatures. Elemental carbon has a

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[12] For a discussion of other refractories see Chapter 21.

melting point assumed to be around 4400° C. It sublimes or volatilizes at approximately 3500° C. For these reasons it is a very good refractory, except in oxidizing atmospheres. Carbon begins to oxidize between 500° and 600° C. In a reducing atmosphere it is better than any of the usual refractories. It is manufactured into bricks and blocks for furnace, hearth, and retort linings. These bricks are made of ground calcined coal or coke, bonded with a tar and pitch binder, and baked to a temperature high enough to coke the binder completely. Carbon articles such as tubes and other shapes are finding increasing application in the chemical industries where unusually severe thermal and chemical corrosion problems must be met.

Carburizers—Carburizers or case hardening materials may be solid, liquid, or gaseous, but the solid materials are used most extensively. The most important are various forms of charcoal, bone char, carbonized leather scrap, crushed bone, horn, mixtures of barium carbonate and charcoal or of various salts and carbonaceous materials. Barium carbonate and charcoal are more efficient than charred leather or wood charcoal.

Commercial products are generally made by grinding the raw materials, mixing them together mechanically with organic binding substances, or in some cases silicates, drying, and baking at low temperatures. Sulfur-bearing raw materials are usually avoided because of their effect on the steel. Particular attention is paid to the screening and grading of the raw materials to obtain certain granular characteristics and mechanical strength in the finished product.

CARBON IN CHEMICAL CONSTRUCTION

The search for more resistant materials of construction for chemical engineering equipment has brought forth many fabricated forms of amorphous carbon and graphite as blocks, rings, adsorption chamber parts, electrostatic precipitator tubes, linings for paper digesters, condenser tubes, heat interchangers, porous carbons for filters, as well as aerator plates. These materials show unusual resistance to chemical attack and corrosive influences. They have shown exceptional performance in connection with acid manufacture, paper making, the electrochemical industries, petroleum oil refining and by-products, as well as parts of machinery operating in chemical plants under severe conditions.

Manufactured carbon shapes show high compressive strengths and good physical properties. Carbon has high electrical conductivity and an extremely low coefficient of thermal expansion. It shows almost universal resistance to chemical action, having found particular application in connection with the highly corrosive fumes of sulfuric, hydrofluoric, and phosphoric acids. Carbon is susceptible to attack by oxygen at temperatures exceeding 600° F. (315.6° C.) and by carbon dioxide and water vapor at comparatively high temperatures. Because of the fact that commercial forms are made up of ground material held together by a binder, the whole mass afterwards being formed or pressed and baked to carbonize or coke this binder, it can be readily appreciated that the particles of carbonized binder form the weakest portion of the shape as far as chemical attack is concerned. Carbon is not immune to destruction by oxidizing agents such as nitric acid, failure occurring because of oxidation of the bonding material. Of the entire group of common reagents, only nascent oxygen, oxygen at temperatures above 625° F. (329° C.), and strong nitric and chromic acids attack carbon.

A satisfactory material of construction must have good physical properties. Those for coke-base carbon (the most common form of the manufactured carbon materials) as determined by the National Carbon Company are shown in Table 4.

TABLE 4—PROPERTIES OF COKE-BASE CARBON

Real density or sp. gr.	2.00–2.10
Apparent density	1.53–1.64
Porosity, %	Approx. 25
Weight per cu. ft., lb. (kg.)	Approx. 100 (45.4)
Tensile strength, lb./sq. in. (kg./sq. cm.)	Approx. 600 (42.2)
Crushing strength, lb./sq. in. (kg./sq. cm.)	6000–9000 (422–633)
Transverse strength, lb./sq. in. (kg./sq. cm.)	3200–6000 (225–422)
Thermal conductivity, cal./cm./° C.	0.00786
Coefficient of thermal expansion per ° C.	0.0000072
Sp. heat, gram cal./gram/° C. at 26–282° C.	0.200
Sp. electrical resistance, ohms per in. cube (per cm. cube)	0.0042–0.0017 (0.00026–0.00010.)
Volatilization point, ° F. (° C.)	Approx. 6300 (3482)
Ash, %	1.00–1.20
Start of oxidation, ° F. (° C.)	625 (329)

As a result of the chemical inertness of carbon, combined with its high strength, new uses in chemical apparatus are developing as rapidly as manufacturers can perfect methods for the production of intricate shapes needed for chemical plants. A large variety of sizes and shapes are at present available for application in chemical apparatus under difficult conditions.

At the present time carbon has shown its suitability in equipment employed in five different fields: (1) acid manufacture, (2) paper making, (3) the electrochemical industries, (4) combustion equipment, and (5) machinery operating under corrosive conditions.

Use in Acid Manufacture—A somewhat spectacular use of carbon has been described by Camp,[13] who states that because of its high electrical conductivity, its lack of a softening or melting point, and its extremely low coefficient of expansion which insures against breakage with sharp changes of temperature, carbon has become standard equipment for Cottrell precipitating units operating in phosphoric acid and sulfuric acid recovery plants. See Figure 7. In the electrothermal production of phosphoric acid, the dense white fume of phosphorus pentoxide is collected as phosphoric acid in a Cottrell precipitator. Considerable quantities of hydrofluoric acid are present in the furnace gases. These are unusually corrosive to most construction materials with the exception of carbon.

Highly corrosive impurities in the sulfur dioxide gas from zinc and copper smelters usually are removed by Cottrell mist precipitators before the gas can be used for contact sulfuric acid. Here again carbon is one of the few satisfactory materials. In other cases carbon tubes have replaced lead tubes, which have the disadvantage of corroding and sagging out of shape at the temperatures employed, in Cottrell precipitators used in connection with drum-type sulfuric acid concentrators in which dilute acid is recovered. Camp states that the carbon tubes are furnished in 6-foot (1.8-meter) lengths with male and female threaded

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[13] Camp, A. D., Chem. & Met. Eng. *37*, 676 (1930).

joints. The tubes range from 7¾ inches (19.7 cm.) inside and 9¾ inches (24.8 cm.) outside diameters to 10 inches (25.4 cm.) inside and 13 inches (33 cm.) outside. The threaded sections allow easy connection.

By the end of 1930 twenty-one Cottrell units equipped with carbon precipitation tubes were in operation in sulfuric and phosphoric acid plants; twenty-three such units containing thirty-six to seventy-two tubes each were employed in connection with the recovery of sulfuric acid from concentrators in petroleum oil refineries or chemical plants. So resistant has the carbon been to corrosive influences that very little if any sign of deterioration can be seen after service of four years in contact with hydrofluoric and phosphoric acids.

FIG. 7. Entire Carbon-tube Installation with Central Electrode Mounted in Place.

Use in Paper Making—In the last few years paper mills have shown an increasing interest in carbon blocks and in carbon linings for paper digesters. Several of these have shown extremely satisfactory records in service, as well as unusual resistance to corrosion. Carbon bricks for lining digesters for the cooking[14] of pulp in either the acid or alkaline process are available. The carbon bricks for digester linings can be secured in standard shapes and sizes, and their practicability has been proved in the field over a period of some five years. In one particular application neither erosion nor corrosion is present, nor is spalling encountered, whereas the previous materials used to line digesters have been subject to these three disadvantages. Previously the shells in the latter plant had been lined at least once a year, owing to the severity of the cooking schedule, and it now appears that the life of the present carbon lining will be indefinite. Other carbon linings have been ordered by pulp producers, and some of them are now being installed.

Up to 1928 the pulp producers objected to black lining materials in digesters

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[14] For a discussion of the cooking of pulp see Chapter 37.

because it was thought that this would be a source of contamination. At this time experimental carbon patches were installed, and after service of two years were found to be satisfactory in that no chipping, spalling, erosion, or corrosion difficulties were met, and that the corners of the carbon bricks were still sharp. Ceramic bricks, on the other hand, always showed disintegration in proportion to their length of service. The carbon bricks were clean, whereas the ceramic bricks were coated with crusts which flaked off and entered the pulp. A kraft pulp manufacturer, who was troubled with relatively short-lived digester linings, in his search for more satisfactory materials employed a complete carbon lining. After service of six months it showed no deterioration and, over this period, no contamination of the pulp. A similar condition was found after service of a year.

Some of the plants in the paper industry, because at the present time very costly equipment is used where constant replacement needs to be made, are experimenting with carbon tubes for heat interchangers to compete in one case with expensive tantalum. To date, the experiment has been a successful one. A new development is the production of impervious chemical carbon pipe which will be impervious to liquids and gases within practical pressure limits as established by industry at present. Tests of this material extending over a two-year period have indicated the resistance of the new material to corrosion and to thermal shock. Fittings for this substance have been developed.

Manufactured carbon lumber for building the sides of buildings where corrosive conditions are particularly severe is now produced. Carbon beams and carbon roof materials of slabs are also available. In this connection, carbon can successfully compete with wood when all the economic factors of the situation are considered.

Use in Combustion Equipment—Carbon has a melting point assumed to be around 4400° C. It sublimes or volatilizes at approximately 3500° C. Inasmuch as its melting point is considerably above those of the normal metal oxides used for furnace linings except in oxidizing atmospheres, carbon is a good refractory. It begins to oxidize between 500° and 600° C. In a reducing atmosphere it is better than any of the usual refractories.

For certain types of furnaces a current-carrying bottom is required. The material largely used for this purpose is a mixture of ground carbonaceous materials with a binder like tar or pitch. The mass is tamped into place and baked, giving a hard product.

Some electrode manufacturers produce carbon paste as a commercial product. This is made of crushed calcined materials screened to a certain predetermined size and mixed with a proper amount of binding material. The binding material is varied according to the use to which the product is to be put. This material is sold in small lots, bagged for shipment, or in carload quantities. Before use, it is heated to make it plastic.

Carbon blocks are generally used for furnace linings and furnace bottoms, particularly in large open furnaces or in places where greater structural strength is desired than would be formed by a monolithic lining.[15] The blocks, being preformed and baked, are denser than the carbon paste and offer greater resistance to oxidation. Blocks are manufactured in practically all square electrode sizes

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[15] Mantell, C. L., "Industrial Carbon," D. Van Nostrand Co. (1928).

They are set up in the furnace like ordinary refractory bricks with the exception that the bond used is carbon paste instead of refractory cement.

A number of standard shapes of the same dimensions as refractory bricks are marketed. These bricks and blocks are made of ground calcined coal or coke, bonded with tar and pitch, and baked to a temperature high enough to completely coke the binder.

The use of carbon refractories allows the possibility of furnace linings being able to resist temperatures at which ordinary refractories would either melt, spall, or lose their valuable properties. Other than carbon, commercially we have no refractories useful above approximately 2700° C. Furnace linings and slag floors in high-pressure boiler furnaces where pulverized coal is used, represent two other recent developments. This material has stood up remarkably well in this service, and no iron precipitate on the surface of the carbon, due to the release of carbon dioxide gas, has been noted after some three years of operation. The carbon is only slightly attacked, and a floor which was built of 8 inch (20.3 cm.) thick slabs appears to have an indefinite life.

Fig. 8. Section of Carbon Floor in Slag Pit of Furnace Burning Powdered Coal.

Electric furnace graphite is unique among refractories because of its purity, low linear expansion, and non-fusibility—all of which permit it to retain its shape, size, structure, and physical properties under conditions of extremely high temperature.

Use in Machinery Operating under Corrosive Conditions—In chemical machinery, particularly in pumps carrying corrosive liquids, carbon or graphite impellers have been quite successful in experimental work to date. Graphite or carbon bearings under extremely corrosive conditions have functioned satisfactorily. Bushings, gaskets, and packings can be made to withstand almost any conditions under which metals or other materials sooner or later fail. Among the new developments has been the manufacture of carbon pipe which will stand liquids under appreciable hydrostatic head. It is expected that this new form will find increasing application where other materials fail.

Industrially, fabricated forms of amorphous carbon and graphite, because of their unusual resistance to chemical attack and corrosive influences, deserve greater consideration as a material of construction for reaction equipment than they have received to date. New applications will be made when the valuable properties of fabricated forms of carbon are more widely appreciated. The material has shown exceptional performance in connection with acid manufacture, paper making, the electrochemical industries, petroleum industries, combustion equipment, and as parts of machinery operating in chemical plants under severe conditions.

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CHAPTER 19

INDUSTRIAL GASES

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This chapter will deal with those industrial process gases which are either consumed immediately as made, such as producer gas, blue water gas and the various oil gases, or are shipped to consumers in the compressed form such as hydrogen, oxygen and acetylene.

PRODUCER GAS

The gas formed by the partial combustion of carbonaceous fuel with air is known as producer gas and is one of the earliest gases to be used for industrial heating. While producer gas was known as such probably as early as 1840, its active development is directly connected with the operation of the open-hearth process[1] for the manufacture of steel, which development had its real start with the invention of the recuperative furnace by Siemens in 1861.

Since almost any material containing 50 per cent of combustible carbon can be gasified in the producer, the fuels used have been of the widest variety, from anthracite coal to straw.

The producer consists of a steel shell lined with fire brick and provided with some means of supporting the fuel bed, with devices to admit air and steam, with suitable means to introduce fuel at the top and to remove the ash and clinker at the bottom, and take off the gas produced. The dimensions may vary from 6 to 12 ft. in internal diameter and from 10 to 15 ft. in height.

Reactions Involved—When air is passed through a bed of ignited fuel, the oxygen of the air combines with the carbon, probably by two reactions:

$$2C + O_2 = 2CO + 58.8 \text{ Calories}$$

and

$$C + O_2 = CO_2 + 97.65 \text{ Calories.}$$

These reactions are also related by the reaction:

$$C + CO_2 = 2CO - 38.85 \text{ Calories.}$$

It is usually considered that carbon dioxide is the first product of combustion and that the carbon dioxide so formed reacts with carbon to produce carbon monoxide. Probably the two gases are formed simultaneously. Table 1 shows the relative amounts of the two gases that are in equilibrium with carbon at various temperatures.

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[1] See Chapter 23.

TABLE 1—EQUILIBRIUM CONDITIONS FOR REACTION

$$C + CO_2 = 2CO$$

Temperature	*Per Cent CO_2*	*Per Cent CO*	*Per Cent N_2*
750° F.	20.6	0.9	78.5
930	17.1	6.4	76.5
1110	10.1	18.1	71.8
1290	3.1	29.4	67.5
1470	.6	33.7	65.7

Reaction with Steam. It will be noted that the combustion of carbon with air is a strongly exothermic reaction and that the temperature in the fuel bed rises to such a point that the ash in the fuel would be fused, with the resulting formation of troublesome clinker. In order to control the formation of this clinker, steam is introduced with air and this reacts with carbon, thus:

$$C + H_2O = CO + H_2 - 28.8 \text{ Calories}$$

and

$$C + 2H_2O = CO_2 + 2H_2 - 18.8 \text{ Calories.}$$

These two reactions are connected by the well-known water-gas reaction:

$$H_2O + CO = H_2 + CO_2 - 10.0 \text{ Calories.}$$

It will be noted that these reactions are both endothermic and that by properly proportioning the amount of steam or water vapor added, the temperature in the reaction zone may be controlled. In an actual producer fuel bed the temperature measurements indicate a variation from 400° to 500° F. at the lower portion of the fuel bed; up to 1900° to 2000° F. in the active zone; dropping again to 1000° to 1300° F. at the top.

Rate of Reaction. The rate of reaction, however, between steam and carbon is very much slower than the rate of reaction between oxygen and carbon. Equilibrium studies of the water-gas reaction are of interest in certain types of processes. The composition of the gas formed in actual producer practice is such as to indicate that the reaction probably does not have opportunity to come to equilibrium, so that the time factor is of importance in determining the composition of the resulting gas.

This subject has been studied at some length by Clement and Haskins and some of their results indicate that in the average commercial producer the time may vary from 1 to 3 seconds.

Apparently at temperatures up to 1600° to 1900° F. the reaction is

$$C + 2H_2O = CO_2 + 2H_2,$$

while at temperatures above 2200° F. the reaction

$$C + H_2O = CO + H_2$$

predominates.

Producer Efficiency—As in the case of carbureted water gas, we have in producer practice the same conflicting requirements. The higher the temperature of the fuel bed the more rapid will be the rate of combustion and the greater the capacity of the apparatus. At the same time, at this higher temperature there is a greater tendency for the formation of clinker with its attendant disadvantages. In general, the character of the fuel determines the economic rate of combustion and the relative amount of steam required. A further point, that is worthy of some consideration from a theoretical standpoint, is the fact that where producer gas is utilized with regenerative furnaces, the amount of steam passing out of the producer should not be in excess of that in equilibrium with the water-gas reaction at the temperature of the recuperators.

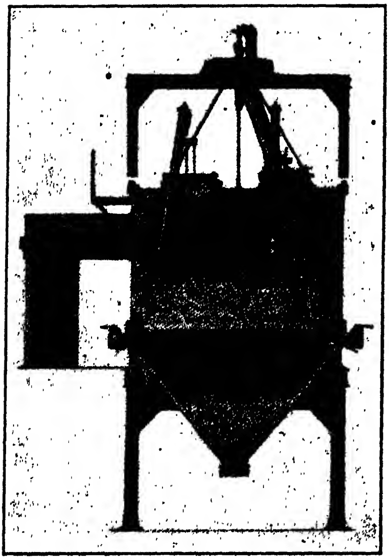

FIG. 1. Typical Gas Producer.

The amount of steam used per pound of fuel may vary from .2 lb. to 2.5 lbs. but in ordinary practice it will rarely exceed .5 lb. per pound of fuel, while the most efficient results appear to be obtained with from .25 to .35 lb.

While it is frequently claimed that a producer will return over 90 per cent of the heat of the fuel in the gas, it may be well to point out that there is no uniformity in the method of expressing efficiencies. It is well known that in a calorimeter, the hydrogen in the fuel is burned to water and the water is condensed so that the latent heat of evaporation is credited to the fuel; whereas in a furnace, the water escapes as a vapor and this latent heat is not recoverable. The available heat in the fuel, therefore, may be expressed differently, either with or without the latent heat of the evaporation of water.

Basis of Calculation. All gaseous fuels containing hydrogen will yield a different value, depending upon the final temperature of the products of combustion; for example, hydrogen will have a heating value of 326.2 B.T.U. per cu. ft. with all the products condensed, while with products in the form of vapor, the value will be 276. Methane will vary from 1009 to 909, while carbon monoxide will have the same value 323 in both cases. A further point is the fact that when producer gas is used at the temperature at which it leaves the producer it will carry from 15 to 17 per cent of its total heat as sensible heat, whereas, should the gas be cleaned and cooled before use, this heat will be lost. Considerable care must be taken, therefore, in comparing the figures on producer efficiency to insure that the methods of calculation are comparable.

In considering the possible losses of fuel by gasification in a producer, we must consider the moisture in the fuel. Under normal conditions this will be rather small, yet where excessive amounts of moisture are present it may become of some importance.

Where producer gas is cooled and cleaned, the tar removed will have a considerable effect on the heating value, as the tar will usually average about 15,500 B.T.U. per lb., and from 3 to 5 per cent of tar is commonly recovered from producer gas made from bituminous coal.

A relatively small amount of fuel is lost by being carried over mechanically and there is also some carbon deposited as soot. These losses would hardly reach a total of more than 3 per cent. There is, of course, a certain amount of combustible carbon lost in the ash. This can be reduced by careful operating conditions, but the higher the original ash in the coke the higher will be the carbon loss, which may run from 1.5 to 3 per cent.

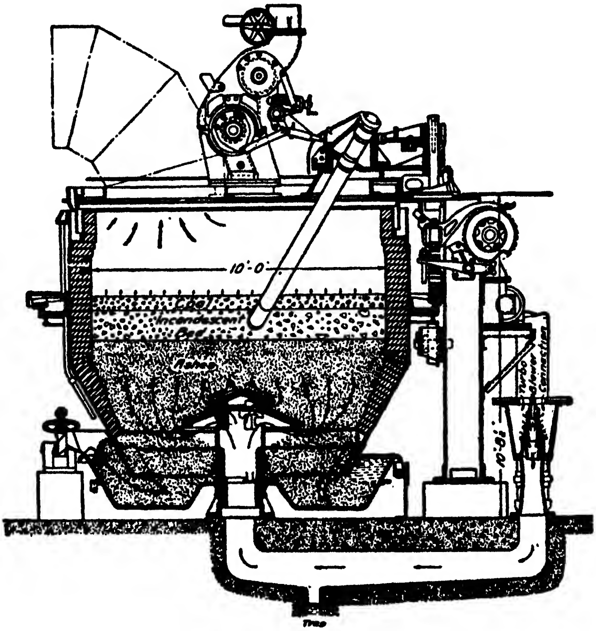

Fig. 2. Producer with Mechanical Grate.

With the modern producer construction the loss by radiation and convection will probably run from 1 to 2 per cent. Summing up, we would have a probable loss inherent in the process of from 8 to 10 per cent. If we add to this the loss due to sensible heat in the gas, we find that we cannot expect an efficiency with cold gas greater than from 73 to 75 per cent, while with hot gas, it may reach 90 to 92 per cent.

Types of Producers—The design of producers varies widely, depending upon the type of fuel to be used and upon the method of operation.

There are three distinct types of producer operation.

1. The type of operation which endeavors to purchase a gas containing as small an amount of condensable vapors as possible.
2. The type of operation which endeavors to produce as large yields of tar as possible.
3. The type of operation which has for its object the production of the maximum yield of ammonia.

We may add to these the slagging type of producer that has had some use abroad, but which has not been used commercially in this country. In this type the clinker is formed as a slag and is tapped off from the bottom in a molten condition as in a blast furnace.

All of these methods require certain modification in design, which in its simplest form would be a steel shell lined with fire brick, provided with a grate, doors for the removal of ash at the base, a charging hopper at the top and a gas take-off. Such producers are operated in small sizes with fuels such as anthracite, where the fusing temperature of the ash is so high that trouble from clinker is practically eliminated.

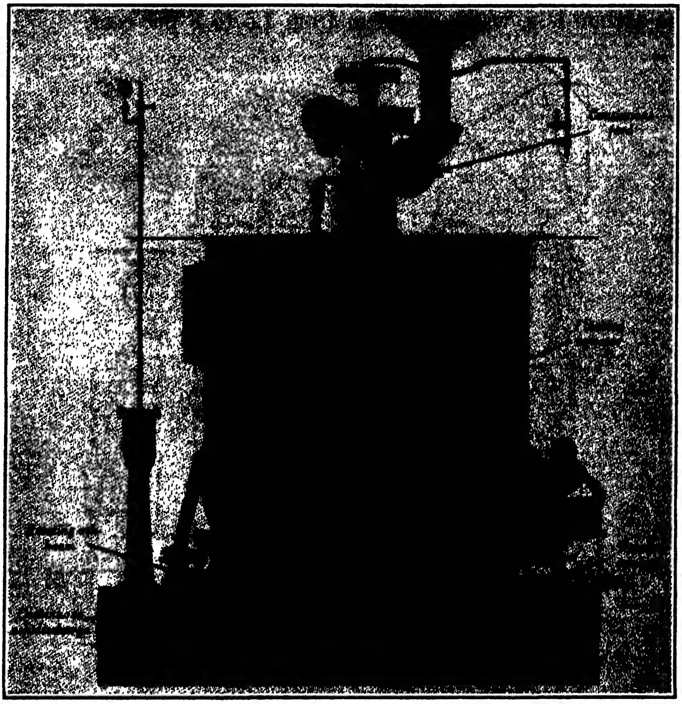

FIG. 3. Producer with Water-sealed Ash Discharge.

Ash Removal. In order to facilitate the removal of the ash, various types of mechanically-operated grates have been used. One type is shown in Figure 2.

When clinker is more of a problem, the bottom of the producer is sealed in a water-filled ash pan and the blast is introduced through a tuyère in the center. In this manner, the clinker is quenched with water and thereby softened so that the removal is simplified and the ash is removed while the producer is in operation. Such a type is shown in Figure 3.

Maintaining a Uniform Bed. With the use of bituminous coal that has a tendency to coke it is found that some method of agitating the fuel bed is desirable to keep a uniform condition. This advantage has been secured in several ways, the most common being when the top of the bed is stirred by means of water-cooled arms. Figure 2 shows one type of water-cooled arm and Figure 3 shows another.

In order to keep the fuel bed in more uniform condition, mechanical devices have been used that will continuously agitate it and at the same time remove the ash. One method of securing this is to rotate the whole body of the producer, the top remaining stationary and provided with a water seal, while the base of the producer may be either stationary or allowed to rotate at intervals with the ash. In a producer of this type, which is shown in Figure 2, the stirring arm operates in a single plane while the fuel bed is rotated beneath it. A steel plate lifts the ashes from the base and discharges them over the side. Figure 4 shows a type of producer in which the main body of the producer is so fixed that the grates rotate. In this design the clinker is prevented from adhering to the walls of the producer by using water-cooled steel plates in the combustion zone. This results practically in a steam boiler around the producer.

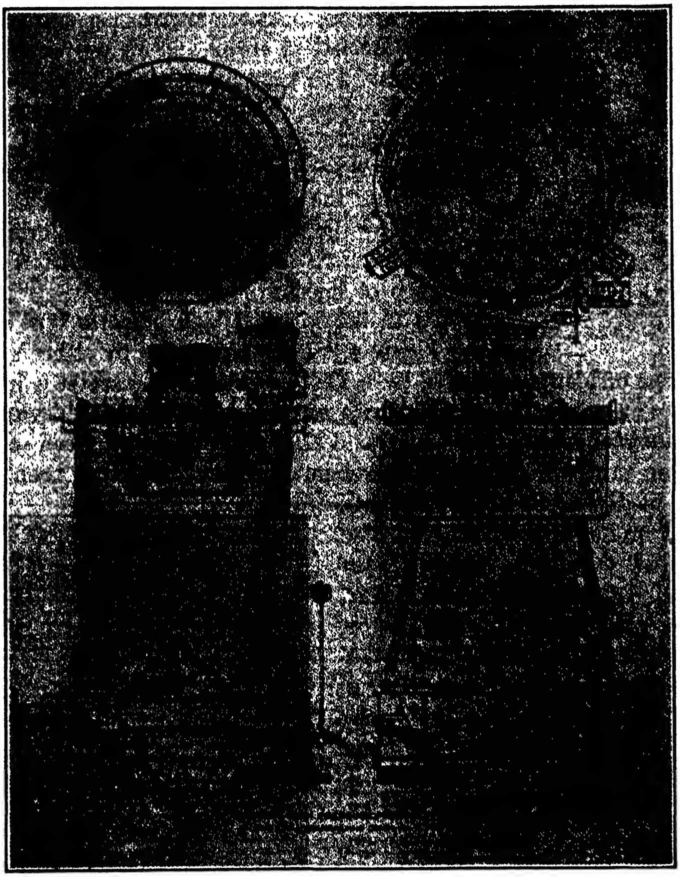

Fig. 4. Producer with Rotating Grates.

Producers of this type are being extensively used for heating retort benches and coke ovens. Since they usually operate on small sizes of coke, there is no necessity for agitating the fuel bed at the top.

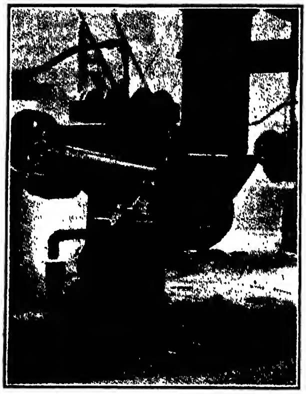

Fig. 5. Automatic Fuel Feeder.

Introducing the Materials. The continuous introduction of the fuel is secured by mechanical devices such as those illustrated in Figures 5 and 6; automatic feeding devices for these are shown in Figures 2 and 3.

The methods of introducing and controlling the amount of steam and air are usually of two types. The type more generally used is known as the low-pressure type which consists of an air injector operated by a steam jet. In this manner both steam and air are controlled by varying the pressure applied at the injector jet and by the use of various sizes of orifice in the jet proper. Figure 2 shows one form of this type of injector.

In the so-called high pressure type shown in Figure 4, the air is supplied by either a fan or a positive-type of blower regulated by a Venturi meter. The steam is introduced separately and is usually provided with some form of metering device.

Efficiency of Operation—A great deal of study has been given to methods of operation that will secure the maximum efficiency This has been found in general to be dependent upon the maintenance of uniform conditions in the fuel bed and a uniform supply of air and steam. In many cases, the fusing point of ash is the determining factor in the amount of steam that must be admitted in order to keep the ash in a sufficiently friable condition for easy removal. At the same time the temperature at the lower part of the fuel bed must be sufficiently high so that an excessive amount of unburned carbon is not lost in the ash.

Satisfactory CO_2 indicators are now available, and the percentage of CO_2 is a very accurate index in the general operation of the producer. Calorimeters are also available that will successfully handle the low heating-value gas produced. In one form, a certain amount of hydrogen is added to insure uniform combustion conditions.

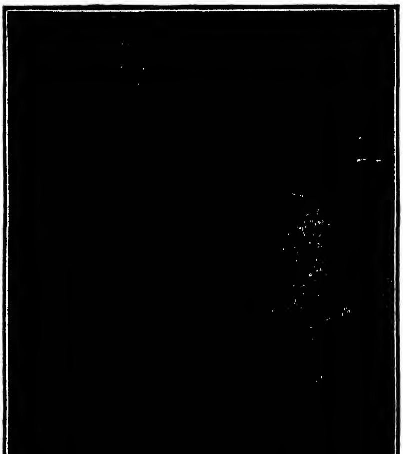

Fig. 6. Automatic Fuel Feeder.

The Zones of Operation. In normal operation there are three well-recognized zones in the producer pile. The top zone is fuel, which is undergoing distillation, the second zone is that of active combustion, while the lower is the ash zone. By introducing iron rods into the fuel bed at the top, the approximate depth and condition of these zones can be ascertained. It is usual to carry the distillation zone from 6-in. to 12-in. depth, the zone of active combustion from 12-in. to 20-in., and from 6 in. to 10 in. of ash. The depth of the distillation zone will vary, depending on whether the gas is to be quite free from tar vapors or whether the tar vapors are not objectionable. In cases where the gas is to be used hot, the distillation zone may be increased to from 12 in. to 18 in. while the active zone is decreased to 6 in. to 8 in.

In considering the actual operation of producers, it appears, therefore, that the efficiency is some function of the rate of combustion per square foot, the temperature, and the amount of water vapor used. With lower rates per square foot, lower temperatures can be carried, but the heating value of the gas is increased and somewhat higher efficiency is obtained. This would correspond to the combustion rate of about 20 lbs. per sq. ft. of grate per hour. By increasing the rate per hour up to 35 lbs., the temperatures are increased, the heating value of the gas is decreased and the efficiency is somewhat lowered. Table 2 indicates some operating results which have been considered satisfactory under the conditions.

TABLE 2—PRODUCER OPERATING DATA

Coal	*Bituminous*	*Bituminous*	*Bituminous*	*Coke*	*Low Temperature*
Per cent volatile	35.0	31.0	32.0	2.7	36%
Per cent ash	5.65	4.60	7.0	16.4	5.5%
Pounds coal per sq. ft. of grate	16.9	31.4	24.00	26.0	26.0 lbs.
H_2O used per lb. coal	.28	.20	2.5	.61	9.4 lbs.
Analysis of gas					
Ill	.4	Nil.	Nil.	Nil.	....
Co	22.6	31.6	11.0	25.7	21.0
H_2	12.6	11.6	24.0	14.4	20.5
CH_4	2.7	3.0	3.0	1.0	4.9
CO_2	5.9	2.4	17.0	7.1	8.3
O_2	.1	......	......	.1	....
N_2	55.7	51.4	45.0	51.7	45.3
B.T.U. high	148.00	169.00	150.00	141.00	183.00
B.T.U. low	138.00	152.00	138.00	132.00	167.00
Efficiency hot	92.33	......	......	89.00	....
Efficiency cold	77.00	76.00	65.00	79.00	78.00
Temperature gas	1400° F.	1250° F.	700° F.	100° F.	300° F.
Sulfate of ammonia, pounds per ton	......	......	80.00	Nil.	80 lbs.
Tar, gallons per ton	......	......	10.0	Nil.	17.8 gal.

Character of the Tar—Where the production of tar as a by-product is desired, the operation is somewhat modified. The height of the distilling zone is very much increased, and the operating temperatures lowered. Producer-gas tar very closely resembles low-temperature tar. In fact, in its chemical characteristics it is more like a crude petroleum than a coal tar. This type of tar has a specific gravity from about .98 to 1.10 and is characterized by a relatively high percentage of tar acids and a rather low percentage of pitch. The tar acids will vary from 13 to 40 per cent and the oil to coke from 60 to 70 per cent. Pitch will run from 27 to 40 per cent. The pitch is usually unsatisfactory when compared with that produced from coal tar.

Typical distillation shows:

	Per Cent
Oil up to 170° C.	.7
Oil up to 230° C.	4.0
Oil up to 270° C.	10.0
Oil up to 300° C.	18.1
Total oil to coke	60.1

Ammonia Production—By greatly increasing the amount of steam used in a producer, the ammonia production can be very greatly increased. This method of operation was developed by Mond. In this scheme, the fuel bed is from 2 to 3 ft. deeper than in the normal producer. The hot gases pass through a heat exchanger whereby the air is superheated so that it will carry about 2.5 lbs. of water per pound of coke. By operating in this manner, about 135,000 cu. ft. of gas is produced per ton of coal, having a heating value of from 135 to 140 net and containing about 80 lbs. of sulfate of ammonia per ton of coal. The gas will have about 11 per cent carbon monoxide, 26 per cent hydrogen, 3 per cent methane, 17 per cent carbon dioxide, 45 per cent nitrogen. While this method of operation has been quite extensively carried on abroad, commercial experiments in this country appear to indicate that while the American coals contain as high a percentage of nitrogen as the foreign coals, the nitrogen apparently must be in a different form in the coal available here, because it has not been possible to increase the yield of ammonium sulfate to that reached with the foreign coals.

Cleaning the Gas—For many heating operations the producer gas is transmitted directly to the furnace in fire-brick lined pipes and is used hot without removing the dust or tar vapors. For use in gas engines for the production of power, the most elaborate cleaning systems are in use which cool the gas and remove all the dust and tar vapors.

Where producer gas is quite dry the dust is usually removed in some form of centrifugal dust catcher similar in design to the separators used to remove condensed water from steam. The removal of the dust is usually all that is done where the gas is used for heating gas retorts or coke ovens. In the more elaborate cleaning systems the gas is washed in towers filled with coke or wooden grids. Centrifugal fans, the P. & A. type of tar extractors and, more recently, the electrical precipitators are used for the removal of the last traces of tar. One system of tar removal that has been quite successful utilizes scrubbers filled with glass wool.

BLUE GAS

Blue gas, or uncarbureted water gas, owing to the high flame temperature that is developed without regeneration or preheating, has found an increasing use in a number of industries. Temperatures up to 3000° F. can easily be reached with modern, direct-fired equipment.

Blue gas has been used for welding where it is particularly valuable, due to the fact that it does not deposit free carbon. For forge work, especially where the heat can be applied directly on the work, the combustion mixture can be readily controlled to prevent the presence of excessive free oxygen. Other uses may be enumerated as follows:

For heat treatment
Muffle furnaces
Enameling ovens
Metal melting
Glass making

One of the most important uses for blue gas has been as a source of hydrogen in the synthetic production of ammonia and, together with carbon monoxide, for the manufacture of methanol.[2]

Apparatus—While the general subject of the production of blue gas has been covered in the manufacture of carbureted water gas, the manufacture of blue gas alone introduces some modifications of the operating procedure, due to the fact that it is not necessary to provide heat for the decomposition of the oil as in the carbureted water-gas process. Figure 7 illustrates a modern gas apparatus without waste heat boiler.

The Operating Cycle. It will be noted that this apparatus consists simply of a generator with stack valves and wash boxes. The production of blue water gas is a cyclical one in which a bed of coal or coke is raised to a predetermined high temperature by a blast of air passing upward through the coke, which portion of the cycle is called the blow, and then by passing steam either up or down through the fuel bed, which portion of the cycle is known as the run. During the first portion of the blow, the oxygen of the air combines with the carbon, primarily to form carbon dioxide, while at the end of the blow when the temperature of the fuel bed has been raised to a high point, a certain amount of carbon monoxide is produced.

The formation of carbon dioxide which takes place according to the equation $C + O_2 = CO_2 + 97.65$ Calories is highly efficient in raising the fuel temperature, while the formation of carbon monoxide $2C + O_2 = 2CO + 58.8$ Calories, not only gives off a relatively small amount of heat but carries from the generator a large proportion of carbon in the form of carbon monoxide.

The rate of gas production depends on temperature; the higher the temperature the greater proportion of steam decomposed with the formation of carbon monoxide and hydrogen; while at the lower temperatures the proportion decomposed is lowered and more carbon dioxide is formed. In the blow portion of the run, the higher temperature of the fuel bed increases the sensible heat of the blast products, resulting in an increased percentage of carbon monoxide with subsequent lowering of the efficiency of this stage of the cycle.

Efficiency. In attempting to secure the maximum efficiency, it has been found that the shorter the blows, the greater the overall efficiency. Short

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[2] See Chapter 30.

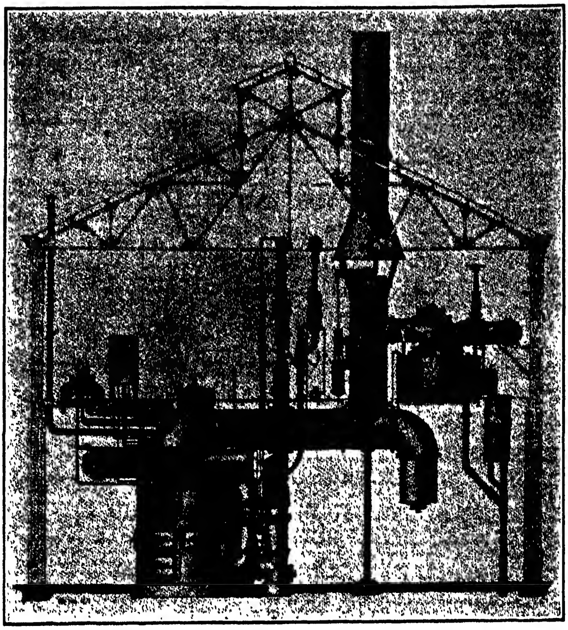

FIG. 7. Blue-gas Set.

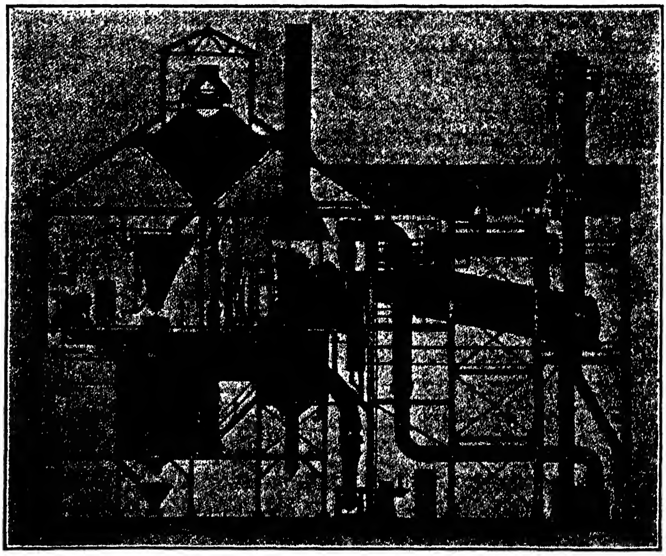

FIG. 8. Blue-gas Set with Waste Heat Boiler.

blows with manual operation were difficult to handle, but with the automatic control the length of the cycle can be very much decreased, and blows as short as a minute or even less are entirely practicable. In this way, the whole fuel bed is maintained at a more uniform temperature and this results in high capacity and decreased trouble from clinkers. By the addition of a waste heat boiler the carbon monoxide that is necessarily made during the blow is ignited and burned in a small vessel in front of the boiler called the ignitor, and the greater proportion of the sensible and latent heat of the blast products is recovered in the form of steam. Figure 8 shows a modern blue-gas apparatus with waste heat boiler. The chamber between the boiler and the generator is the igniting chamber. This is filled with checker-brick and is provided with blast connections to secure complete combustion of the blast gas.

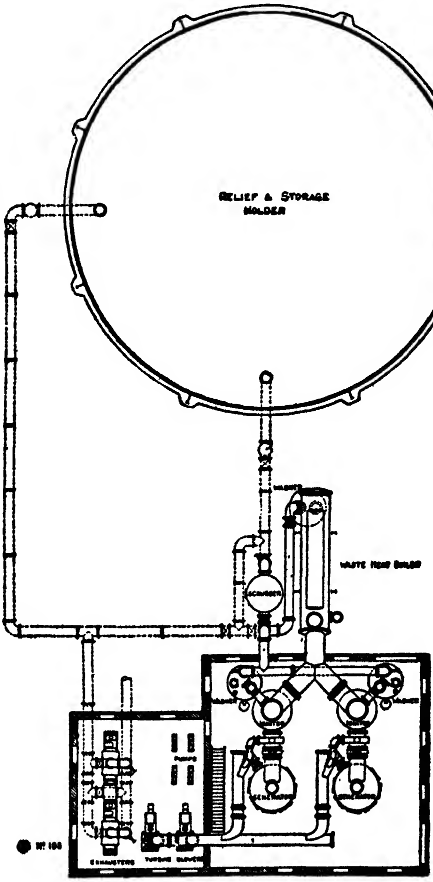

FIG. 9. Layout of Blue-gas Plant.

Coke is the usual fuel for the manufacture of blue gas. Efficient operation calls for 36 lbs. of coke and about 30 lbs. of steam per thousand cubic feet. A typical gas has the following composition:

Carbon monoxide	$CO = 43.5\%$
Hydrogen	$H_2 = 47.3\%$
Methane	$CH_4 = 0.7\%$
Carbon dioxide	$CO_2 = 3.5\%$
Oxygen	$O_2 = 0.6\%$
Nitrogen	$N_2 = 4.4\%$
Specific gravity relative to air	= .559
Calorific value	= .302
Flame temperature (calculated)	= 3470° F.
Specific heat	= .45

Recently, the use of 80 to 90 per cent bituminous coal and 10 to 20 per cent coke has, in some localities, indicated a reduced cost of generator fuel. While the mixture of bituminous coal and coke has slightly reduced the capacity of the machine, the heating value of the resulting gas is slightly higher than that produced from coke alone. This is due to the gases produced by the distillation of coal at the top of the fuel bed.

With the automatic control of blue-gas operation, the variation of temperatures throughout the fuel bed are held within very narrow limits. This results in higher efficiencies, a more uniform quality of gas, and eliminates the difficulty in the removal of clinker. The air and steam used are both metered to insure the proper proportion which is essential for uniform operation. By the use of a waste heat boiler, all of the steam necessary in operating the apparatus can be produced, and by the use of electrically-driven blowers and exhausters, the necessity for fuel-fired boilers is eliminated. Figure 9 is a typical layout of a modern blue-gas plant with waste heat boilers.

COMPRESSED PETROLEUM GAS

The compressed petroleum gas industry has developed rapidly during the past decade and its development has been coincident with the rise in the production of natural gasoline, although at the present time a considerable proportion of the constituents are recovered from the so-called refinery gases resulting from the distillation and cracking of petroleum.

Table 3 gives some of the principal statistics covering the production and use of compressed petroleum gases.

In the early days of the production of natural gasoline large quantities of the low boiling paraffin hydrocarbons were allowed to evaporate into the air and this process was known as "weathering." With a better understanding of the requirements of motor fuel the removal of these gases took place in fractionating columns known as stabilizers which permitted an accurate control over the amount of low-boiling paraffins in the motor fuel.

Properties—Methane and ethane have too high a vapor pressure for commercial use while pentane has too low a pressure for satisfactory use as compressed gas and has a greater value in the motor fuel. There remain, then, *propane, normal butane,* and *iso butane* with the corresponding olefins which form the basic constituents of the petroleum gases. These gases are distributed either as a relatively pure propane—a mixture of roughly 50 per cent propane

TABLE 3—STATISTICS OF PRODUCTION AND USE

1940 U. S. Bureau of Mines

	Thousands of Gallons	*Percentage*
Production		
Propane	109.216	34.8
Butane	77.056	24.5
Mixtures of Propane and Butane	123.348	39.5
Pentane	3.836	1.2
Totals	313.456	100.0
Use		
As Domestic Fuel	134.018	42.7
City Gas Manufacture	20.285	6.5
Industrial Fuel	69.892	22.3
Chemical Manufacture	34.671	11.1
Internal Combustion Engine	53.916	17.2
Other Uses	.672	0.2
	313.456	100.0
Method of Delivery		
In Bulk, i.e., Tank Cars and Tank Trucks	....	78.2
Cylinders and Drums	....	21.8
Totals	....	100.0

and 50 per cent butane which is very widely used, and a relatively pure butane which consists of a mixture of iso and normal butane.

Table 4 shows the general characteristics of these mixtures.

TABLE 4—PROPERTIES OF CONSTITUENTS OF PETROLEUM GASES

	Propane	*n Butane*	*Iso Butane*	*Propylene*	*1-Butylene*	*2-Butylene*	*Iso Butylene*	*Commercial Mixture*
Specific gravity of liquid	.509	.582	.567	.522	.539	.613	.601	.576
Specific gravity of gas	1.521	2.004	2.004	1.479	1.977	1.977	1.977	1.950
Weight per gallon of liquid	4.238	4.854	4.718	4.35	4.99	5.11	5.01	4.8
Weight per cubic foot of gas	.120	.158	.158	.111	.148	.148	.148	.149
Cubic feet of gas per gallon	36.4	31.6	30.7	38.5	32.9	33.7	33.2	32.0
Heating value B.T.U. per cu. ft. gas	2590	3370	3370	2336	3084	3084	3084	3200
Heating value B.T.U. per pound	27661	21308	21308	21041	20840	20840	20730	21420
Lower limit of inflammability	2.4	1.9	1.9	2.0	1.7	1.7	1.7	2.0
Upper limit of inflammability	9.5	8.4	8.4	11.1	9.0	9.0	9.0	6.6
Pressure gauge at 100° F.	172	38	59	228	66	50	63	65

Recovery Methods—Two methods are used for recovering the raw gases. In the *compression* method, the wet natural gas or the refinery gas is compressed and the hydrocarbons recovered by cooling.

In the *absorption* method, which is very similar to that described in a previous chapter,[2a] the natural gas or refinery gas is scrubbed with an absorbing oil, frequently under pressure. The enriched absorbing oil is then heated to drive off the absorbed gases. These are cooled and recovered by condensation and compression.

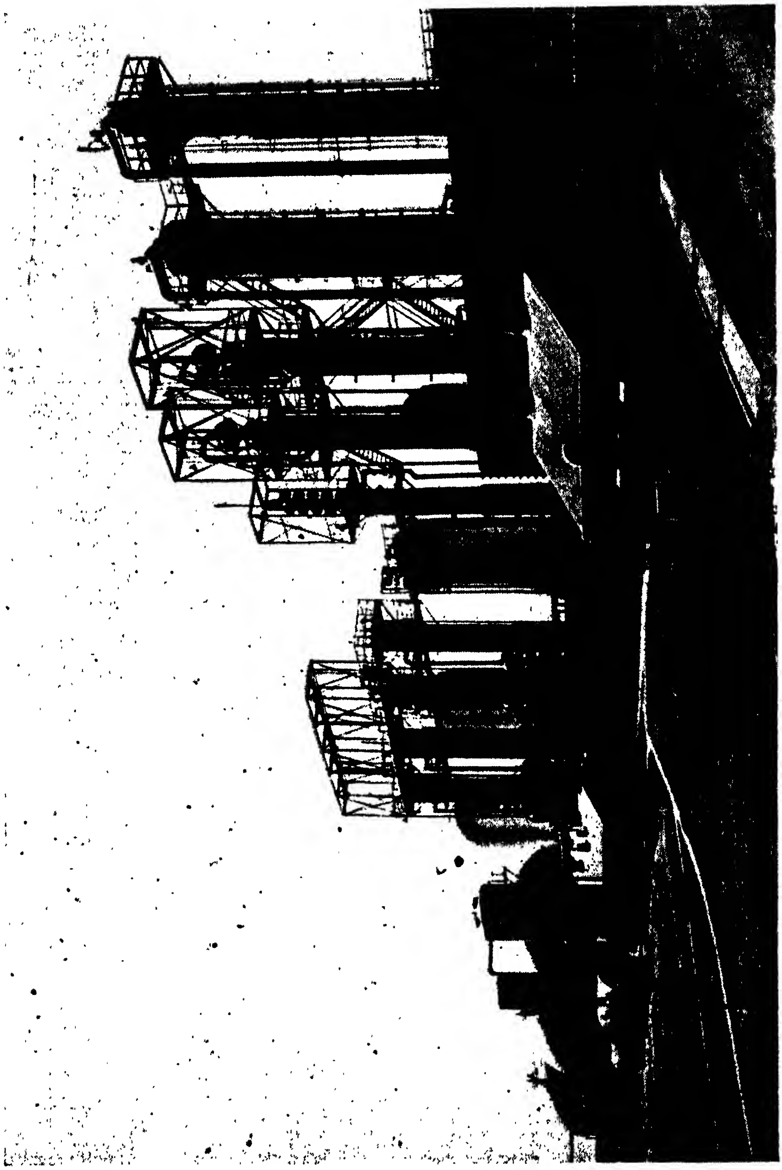

FIG. 10. Plant for Manufacture of Propane and Butane.

The raw material thus obtained is distilled in fractionating columns. These require a very careful control of the temperature and pressure conditions in

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[2a] See Chapter 15.

order to secure close separation of the desired constituents. Figure 10 shows a modern plant for the production of these commercial mixtures.

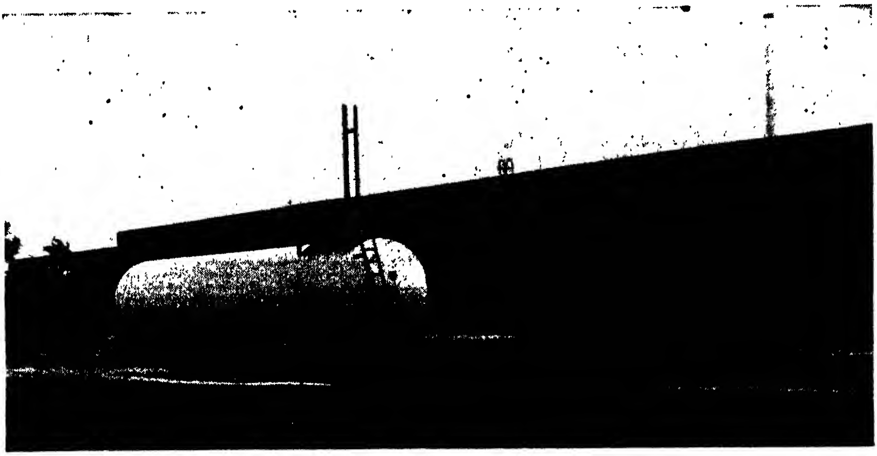

FIG. 11. Tank Car and Storage Tank for Compressed Petroleum Gases.

Commercial Use—As shown in Table 3, propane and butane are used for domestic purposes where they serve to furnish gas service at points far distant from any city gas supply. For this purpose, a mixture of butane and propane is ordinarily employed as this will have a sufficiently low boiling point to evaporate without the use of an external source of heat. The gas is distributed in steel cylinders provided with a reducing valve.

FIG. 12. Butane-air Plant. (Courtesy Philgas Dept., Phillips Petroleum Co.)

For large-scale users the gases are usually shipped in tank cars which have been developed to withstand pressures up to 450 lbs. per square inch. Figure 11 shows one of these cars together with the pressure storage tank that is used as a supply tank.

In certain parts of the country, particularly California, a large amount of compressed petroleum gas is used as a motor fuel and is distributed to local dealers in tank trucks.

Butane-Air—Another use for compressed petroleum gases that has been developing is the distribution of a butane-air mixture of the usual heating value (approximately 530 B.T.U. per cubic foot) for use as city gas. Butane is generally used for this purpose owing to low vapor pressure and is mixed with air with some form of automatic proportioning device. At the present time about 168 plants are distributing such mixtures. Figure 12 shows one of these small plants, the operation of which can be made nearly automatic.

HYDROGEN

For many years, the industrial demands for hydrogen were limited to the relatively small quantities used in operating oxy-hydrogen lamps used for projection purposes and for use in the oxy-hydrogen blowpipe for melting refractory materials.

With the introduction of the hydrogenation process for hardening fat,[3] the development of the synthetic process for the formation of ammonia[4] and methanol,[5] and the use of hydrogen as a reducing agent in the manufacture of certain metals such as tungsten, the demand for hydrogen has increased to such a point that its manufacture has become an important industry. While a certain amount of hydrogen has been used for many years for the inflation of balloons, this has usually been manufactured by chemical processes in portable plants and will not be considered in this chapter.

Early Processes—The early methods for the manufacture of hydrogen were usually chemical, such as the decomposition of acids with metals, usually zinc and sulfuric or hydrochloric acid. Considerable work had been done on the decomposition of steam by metallic iron contained in heated retorts and this process is known as the iron-steam process. It consists briefly in reducing oxide of iron to a metallic state by means of water gas and then passing steam over this iron which is heated externally to about 1200° F.

Iron Steam Process. The following equations are usually assumed to hold in this reaction. The iron oxide is initially assumed to be a metallic oxide, Fe_3O_4, and its reduction to metallic iron takes place in two stages, viz.:

$$Fe_3O_4 + H_2O = Fe_2O + H_2 = 3FeO + H_2O$$

and

$$Fe_3O_4 + CO = 3FeO + CO_2$$

and

$$3FeO + 3H_2 = 3Fe + 3H_2O$$

and

$$3FeO + 3CO = 3Fe + 3CO_2,$$

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[3] See Chapter 41.

[4] See Chapter 8.

[5] See Chapter 30.

or we may summarize the reduction of the iron ore to iron by water gas as

$$Fe_3O_4 + 2CO + 2H_2 = 3Fe + 2CO_2 + 2H_2O - 18{,}000 \text{ calories.}$$

This stage of the process would be called the reduction stage.

The second stage of the process or the making stage may be represented by

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2 + 38{,}400 \text{ calories.}$$

These reactions have been very carefully studied in an experimental way and the relative proportion of hydrogen and carbon monoxide consumed is shown in Table 5:

TABLE 5—Fe_3O_4—FeO—Fe EQUILIBRIUM *

Fe_3O_4—FeO Reaction		*Per Cent CO Used*	*Water Gas : Hydrogen*
Temperature	*Per Cent H_2 Used*		
570° C.	27	47	2.7
650° C.	41	55	2.1
750° C.	58	67.5	1.6
850° C.	75	75	1.33

FeO—Fe Reaction		*Per Cent CO Used*	*Water Gas : Hydrogen*
Temperature	*Per Cent H_2 Used*		
570° C.	27	47	2.70
650° C.	30	44	2.70
750° C.	35	40	2.55
850° C.	38	36	2.70

* Chaudron—Annales de Chemie, 1921.

Due to the fact that the gases probably do not come into complete equilibrium, which is caused by the variable reaction time and by the change in characteristics of both the iron and the water gas, too much reliance cannot be placed on the equilibrium measurements as applied to practical operation, but they are of great interest as indicating the mechanism and course of the reactions.

There is another reaction which may take place that is of considerable importance in connection with the purity of the hydrogen produced; this is the equilibrium between carbon monoxide, carbon dioxide and hydrogen in the sense, $2CO = CO_2 + C$, which indicates that under certain conditions carbon may be deposited on the iron. Since this carbon would combine with steam in the making portion of the cycle and give carbon monoxide, this reaction is to be eliminated as far as possible and several methods of operation have been suggested to avoid the deposition of carbon. One of these proposes the use of a water gas containing a ratio at the temperature of operation so that no carbon would be deposited.

Another system partially burns the blue gas before using it as a reducing agent, while still another system adds a certain proportion of steam to the blue gas in order to prevent the deposition of carbon.

It has been found that the relative occurrence of the impurities in the hydrogen made by the iron-steam process are in accordance with the water-gas reaction, viz., $CO + H_2O = CO_2 + H_2$.

There are several types of apparatus for carrying on the process. These may be divided into two types. In the first, the iron ore is contained in a relatively large number of externally heated retorts, while in the second type the ore is contained in a single large shaft in an internally-heated furnace.

The Lane System. The Lane system is an example of the first type of apparatus which was used in the commercial production of hydrogen. In this system, the generators consist of thirty-six cast-iron retorts, the main portion of which is about 9 ft. 9 in. long, 9 in. internal diameter and 12 in. external diameter. These are set in a furnace approximately 14 ft. 6 in. long, 10 ft. wide and 10 ft. deep. A bench containing thirty-six retorts has a rated capacity of 3500 cu. ft. of hydrogen per hour. The retorts are set in three rows of twelve retorts each and provided with appropriate systems of piping and valves so that three cycles of operation are possible.

Blue gas, which is used as a reducing agent, passes in at the bottom of the retorts and is discharged from the top. From the retorts, the spent reducing gas, which carries a large amount of water vapor, passes to atmospheric condensers, where it is cooled and the greater portion of the water vapor removed. From the condensers it passes through an appropriate system of piping and burners to the interior of the furnace, where it is burned to maintain the temperature necessary for the reaction. It has been found that the reduction phase is much slower than the making portion of the cycle. The retorts are arranged so that while one set is making, two sets will be reducing. In this manner, with three sets of retorts, each retort is on the making cycle every half hour.

At the end of the reduction period, the retorts and piping are full of spent reducing gas, so that when the steam is first turned into the retorts the hydrogen formed drives out the reducing gas and this is allowed to purge for from 15 to 20 seconds. The valves are then changed and the hydrogen passes to the purifying system.

The making portion of the cycle is usually one-half of the reducing portion of the cycle. Twenty minutes' reduction, 10 minutes' make, 20 seconds' purge are the usual running conditions. The rate of production of the hydrogen, however, varies quite widely during the making portion of the cycle. At the beginning of the cycle it is usually from 2½ to 3 times as rapid as at the end. It has been found that by cutting the reduction period to 10 minutes and the making period to 5 minutes that a slightly increased production can be obtained, say, 4000 cubic feet per hour, but the purity is slightly lower.

In order to eliminate the effect of the deposition of carbon in the iron, which lowers the purity due to the formation of carbon monoxide, and also to eliminate any sulfur which may be deposited during the reduction period, it is usual to burn out the retorts with an air blast for 10 or 15 minutes after 8 hours' operation. Under the influence of the air blast the carbon and sulfur are both consumed, but the iron is oxidized so that the burning-out period is followed by a reduction period and the retorts again resume their operating cycle.

As it leaves the retorts the hydrogen may contain several per cent of carbon dioxide and traces of sulfur compounds. These may be removed by several methods of treatment, but for the ordinary commercial hydrogen the gas is purified by condensation and scrubbing and is then passed through purifier boxes containing moistened hydrated lime. This will remove carbon dioxide and traces of sulfur compounds. In order to prevent deterioration of the iron mass, the blue gas used is also purified from traces of sulfur compounds by treatment with hydrated oxide of iron. In the Lane plant there are two benches containing thirty-six retorts each, 2- to 6-ft. blue gas generators, a small holder for the blue gas, 15,000 cu. ft. capacity, and a holder for hydrogen of about 10,000 cu. ft. capacity. The purification boxes for the blue gas consist of four 16-ft. square boxes by 4 ft. deep, while the purification for the hydrogen is carried out in four boxes 10 ft. square and 4 ft. 6 in. deep.

The reduction mass is composed of a carbonate iron ore, which is used in lumps from 4 to 6 in. in diameter at the bottom, graduating to 1½ to 2 in. at the top. Each retort holds about 300 lbs. of ore.

The purity of the hydrogen produced by this process depends somewhat on the cycle of operation and the temperature. Table 6 shows some operating results:

TABLE 6—OPERATING RESULTS, LANE PROCESS

Temperature ° F.	*Make per Hr. Cu. Ft.*	*Reducing Feet*	*Making Feet*	*Purge, Inches*	*Steam per M Lbs.*	*W.G. : H.*	*Purity H_2 Per Cent*
1168	3758	10	5	15	143.5	2.84	99.53
1196	3786	10	5	15	140.7	2.70	99.61
1255	3985	10	5	15	133.7	2.68	99.68
1272	4055	10	5	15	131.5	2.67	99.70

In considering the efficiency of this type of apparatus, the reactions are slightly exothermic, but there is not sufficient heat to bring the products of the reaction up to the operating temperature, so that some of the heat secured by the burning of waste-reducing gas is actually utilized in the process.

The ratio between the water gas used and the hydrogen produced may vary at the higher temperatures from 1.33 to 2.7, but practically it is somewhat higher than this and will usually vary from about 2.25 to 2.4 on fresh oxide to 2.65 to 2.75 on old ore, the average figure being about 2.5.

While the rate of production is somewhat higher and the purity of the hydrogen is also somewhat higher at high temperatures, it has appeared advantageous to keep the operating temperatures between 1150 and 1200° F.

Hydrogen from the Water-Gas Reaction—A common method of producing hydrogen, which utilizes blue gas as its starting point, is that which takes advantage of the water-gas equilibrium. By mixing the blue gas with steam and bringing it in contact with suitable catalysts, the ratio between the carbon dioxide and the carbon monoxide can be changed, so that after the removal of the carbon dioxide by absorption in water under pressure or in solutions of soda ash or ethanol amines, hydrogen of the required purity can be obtained.

The equilibrium condition in the water-gas reaction can be expressed as follows according to Haber:

$$K = \frac{pCO \times pH_2O}{pCO_2 \times pH_2} \text{ or } \log K = -\frac{2232}{T} - .08463 \log T - .0002203\ T \times 2.5084$$

By adding steam to the blue gas we may make the ratio $\frac{H_2O}{H_2}$ so large that the ratio of $\frac{CO}{CO_2}$ will be decreased sufficiently at equilibrium; thus, with the increase in carbon dioxide from the reaction, the percentage of carbon monoxide will be reduced to a satisfactory value. In order that this reaction will be commercially successful, a very active catalyst is required so that the reaction can take place rapidly at a low temperature and a relatively high ratio of steam to hydrogen can be used. It is possible to reduce the carbon monoxide in this process to approximately 1 per cent. The amount of steam to be used depends upon the activity of the catalyst, which is usually some form of iron oxide activated with chromium or thorium. The amount of steam used with fresh material may be as low as three volumes to one of hydrogen and, as the reaction mass becomes less efficient, the steam-hydrogen ratio may be increased to 5 or 6. The reaction when operating in this direction is usually sufficiently exothermic to maintain the operating temperature by the use of a relatively small heat exchanger. This method is said to produce the cheapest hydrogen in the world and some very large-scale plants are in operation.

Another method of treating water gas consists in passing the gas over calcium oxide at a temperature of 900° to 1000° F. The calcium oxide removes the carbon dioxide even at this temperature and, although the $CO_2 - CO$ ratio is not changed, the absolute percentage of CO_2 may be reduced to a very low figure for CO. By operating in this manner at 950° F., the CO may be reduced to as low as .2 per cent, and it is claimed that a hydrogen content of 97½ per cent can be obtained. The amount of lime required is naturally quite high and the fact that it would disintegrate rapidly in handling may be a serious disadvantage in the technical operation of this process.

Refrigeration Method—Considerable work has been done in Germany on the purification of blue gas for the production of commercial hydrogen by fractional distillation of the liquefied product. After preliminary purification from H_2S, CO_2 and water vapor the gas is liquefied in a column similar to that described under the manufacture of oxygen. Advantage is taken of the difference in the boiling point or the constituents. Carbon dioxide boils at −78° C., CO at −190° C., N_2 at −193°, while H_2 boils at −252° C. In this manner, the H_2 may be separated at a purity of 97 to 97½ per cent, with 1.7 to 2 per cent of CO_2 and from 1.8 per cent of N_2. The CO that is produced is usually utilized in internal combustion engines as a source of power.

Thermal Decomposition of Hydrocarbons—The thermal decomposition of hydrocarbons has also been utilized to produce hydrogen, but the hydrogen thus formed has usually been of relatively low purity. A German process utilizes acetylene, while ordinary coal gas passed through the generator of a blue-gas apparatus can be decomposed to form hydrogen having a purity of about 80 to 82 per cent. By decomposing oil in an apparatus similar to that used for the manufacture of carbureted water gas, about the same degree of purity can be obtained as with acetylene; while with special apparatus provided with very high melting-point refractories and utilizing a very pure form of carbon as fuel, it is possible to secure a gas of the following composition:

	Per Cent
Hydrogen	96.3
CO_4	2.3
Methane	1.2
Nitrogen	0.2

In order to secure gases of this purity, it is necessary to operate at very high temperatures in what would correspond to the carburetor of a carbureted water-gas set. These temperatures are approximately 1500° to 1600° C. and at such temperatures it is difficult to prevent the disintegration of refractory materials.

At the present time an important source of hydrogen for many of the hydrogenation processes which do not require exceptional purity utilizes the simple thermal decomposition of any hydrocarbon vapor into its elements. For example, large quantities of hydrogen are made by the decomposition of natural gas and still gases from petroleum refineries. In certain instances the supply of natural gas can be obtained very cheaply and this permits the use of such a process as a very economical source of hydrogen.

Electrolysis of Water—When the hydrogenation of oil was first introduced, it was believed that very high purity of hydrogen was required and the hydrogen was generally produced by electrolysis. The power requirement, governed by the electromotive force, depends upon the electrodes and the solution. With platinum electrodes, the voltage should be about 1.23 volts, but due to the phenomenon known as over-voltage, about 1.7 volts are actually required with platinum electrodes and a solution of sodium hydroxide. Both iron and nickel have a slightly lower over-voltage, of the order of .08 to .12 volt, so that apparently a nickel-plated anode and an iron cathode represent the most practical commercial materials.

The figures quoted for E.M.F. apply to commercial cells where it is necessary to overcome certain resistances in the cell itself. In order to overcome this resistance, additional voltage must be used so that from 2 to 4 volts are required per cell to secure the required flow of current. Theoretically, therefore, we may expect that 1 kilowatt hour will produce about 9.408 cu. ft. of hydrogen and 4.704 cu. ft. of oxygen. Practically, we do not expect to secure more than 3½ cu. ft. of oxygen and 7 cu. ft. of hydrogen per kilowatt hour.

Cell Design. In order to separate the gases produced at the anode and cathode the design of the cell must be such that the gases are either separated by a diaphragm or that the electrodes be so placed that no mixing can take place. The Schuckert cell is of the latter type, while the usual cell has a diaphragm made of asbestos separating anode from cathode; so that, while it will not permit the passage of gas, it is sufficiently porous not to greatly increase the resistance.

Purity. The purity of the hydrogen produced by electrolysis is usually from 99.7 to 99.8 per cent and the oxygen is usually somewhat lower—from 99.3 to 99.5 per cent. Before the present commercial demand for oxygen, it was usually a by-product in the manufacture of hydrogen and thus the cost of generating hydrogen by electrolysis was very high, but the present demand for compressed oxygen has been of material assistance in lowering the cost of electrolytic hydrogen.

Bergius Method—Another method has been proposed for manufacturing hydrogen, that, while it has considerable theoretical interest, may prove to be quite practical. This is a process proposed by Bergius, in which he treats very pure carbon or finely-divided iron with water under high pressure. The presence of some catalyst is required which, in the case of carbon, is usually thallous chloride, while in the case of iron, ferrous chloride or copper is used.

At a temperature of 640° F. and 150 atmospheres' pressure, the iron reacts quite rapidly with water according to the reaction $3Fe + 4H_2O = Fe_3O_4 + 4H_2 + 38.4$ calories, so that, from a thermal standpoint, the process would be self-sustaining. At these pressures and temperatures, however, the manufacture of the autoclaves is a very serious problem. It is assumed that 1 cu. ft. of reaction space will yield 150 cu. ft. of hydrogen per hour, while the purity is said to be extremely high. This purity, however, must undoubtedly be a function of the carbon content of the iron used. Table 7 summarizes the qualities of hydrogen normally produced by different processes.

TABLE 7—PURITY OF HYDROGEN BY VARIOUS PROCESSES

Process	*Purity of Hydrogen Per Cent*
Decomposition of oil water gas apparatus	80.0 to 82.0
Decomposition of oil special apparatus	94.0 to 96.0
Shift of water-gas equilibrium	96.0 to 97.0
Liquefaction of blue water gas	97.0 to 97.5
Iron steam process (Lane)	99.5 to 99.7
Electrolysis	99.6 to 99.8

In considering the choice of a process for the production of hydrogen, the quality required and the nature of the impurities present must be given consideration. For aeronautical purposes the purity is not of great importance, 90 per cent hydrogen being entirely satisfactory. The principal impurity to be guarded against is oil vapors which would attack the rubberized fabric. For the hydrogenation of non-edible fats, the principal impurities to be guarded against are sulfur, oxygen and carbon monoxide, although recent experiments appear to indicate that the catalyst can be adapted to gas of much lower purity than the earlier work would indicate. For the reduction of metals, carbon compounds are the most serious impurities, as they tend to form carbides.

Removal of Impurities—The synthetic production of ammonia demands the very highest purity and while nitrogen here would not be an impurity, the carbon monoxide, oxygen, and moisture must be carefully removed.

For ordinary hydrogenation work, the use of lime in the usual form of box purifiers has been found satisfactory. Where still higher purity is required and, especially where the gas must be used under fairly high pressure, it can be scrubbed with water at 20 to 30 atmospheres or where low pressure purification is required, solutions of sodium or potassium hydroxide are used in either mechanical or tower scrubbers. Hydrogen sulfide is usually removed in iron-oxide purifiers or by liquid purification as described in Chapter 15. Traces of carbon bisulfide are removed by treating the gas with a catalyst, which is iron oxide or iron and chromium, which changes the carbon bisulfide to hydrogen sulfide. This is then removed with iron oxide.

Carbon monoxide is removed by a variety of methods, depending upon the purity required and upon the process. Small amounts of it may be changed to methane by treatment with a nickel catalyst, if methane does not interfere with the further use of hydrogen; or it may be oxidized by a catalyst by the process known as preferential combustion by mixing about twice the theoretical oxygen required and passing it over copper oxide or a suitably activated iron oxide. This process requires very careful operation as there is a very narrow temperature range of about 100° F. where the carbon monoxide will be oxidized in preference to the hydrogen. Owing to the loss of hydrogen, this process would not be economical where the carbon monoxide exceeded, say, 1 to 1½ per cent. The carbon monoxide may also be lowered by treatment with soda lime at 500° C., as mentioned in the description of the catalytic reduction of hydrogen from water gas.

For the removal of the last traces of carbon monoxide in preparing hydrogen for the ammonia synthesis, ammoniacal cuprous chloride or carbonate solutions are used under very high pressures, say, 200 atmospheres. The solution is regenerated and the carbon monoxide recovered by releasing the pressure and heating to between 70° and 80° C.

Methane is very difficult to remove, but generally it merely serves as an inert gas and must be blown off as it accumulates.

Analysis. In the analysis of hydrogen, there are a number of methods, depending upon the degree of accuracy required. For works control, the specific gravity balance gives rough relative indications. These may be checked by combustion of the hydrogen with the usual form of gas analysis apparatus. Thermal conductivity methods are also used. This method determines the difference in the thermal conductivity of gases by passing the gas under test around a thin wire carrying current while a gas of known purity is passed around a similar wire. These two wires form two arms of a Wheatstone bridge and the change in the rate of cooling which is measured by the change in resistance is a measure of the gas composition. Hydrogen has a thermal conductivity of 10.4, while nitrogen, carbon monoxide and methane range from 5.24, 4.99 and 6.47 so that the method may be made quite accurate.

Carbon monoxide can be determined in the presence of hydrogen by preferential combustion, and, by determining the carbon dioxide by conductivity methods, this method has been made the basis of a carbon-monoxide indicator.

Oxygen can be determined by the regular gas-analysis methods. Phosphorus is usually determined by burning a relatively large amount of gas and determining the phosphorus as phospho-molybdate. The same type of apparatus as used for the determination of fixed sulfur in city gas may be used for other sulfur compounds.

ACETYLENE

Acetylene as an illuminant has become obsolete but the use of acetylene for welding and cutting has become very large. Acetylene is manufactured by decomposing calcium carbide with water, usually in some form of automatic apparatus. Calcium carbide[6] is manufactured in the electric furnace by fusing a mixture of lime and coke. Although acetylene was known chemically as far back as 1836, and in 1862 the formation of calcium carbide was discovered by Woehler, it was not until Wilson's discovery in 1892 that calcium carbide could be commercially manufactured in the electric furnace, that acetylene became of any importance.

Manufacture of Calcium Carbide—In the manufacture of calcium carbide, the purity of the raw materials is of great importance and much of the success in the commercial use of acetylene can be attributed to the care taken and the chemical control exercised in the manufacture of the carbide. After fusion in the furnace, the carbide is crushed, sized, and packed in hermetically-sealed cans. Calcium carbide as formed in the electric furnace is a hard crystalline substance of grayish color and weighs about 138 lbs. per cubic foot. It is usually packed in cans holding 200 lbs. The commercial sizes for large generators are 3½ in. to 2 in. and for lamps 1 in. to ½ in. and some other smaller sizes running down to dust.

While pure carbide should yield about 5 cu. ft. of acetylene per pound, the yield of gas varies with the size. The larger lumps yield considerably more gas per pound.

Formation of Acetylene—The formation of acetylene from the carbide takes place according to the following reactions:

$$CaC_2 + H_2O = C_2H_2 + CaO \quad \text{and} \quad CaO + H_2O = Ca(OH)_2.$$

However, this reaction does not take place below —5° C. The reaction is exothermic, the net result being about 29.1 large calories. This heat of formation is very important as it must be taken care of in a design of the generator. Acetylene polymerizes readily at 600° C. into benzol, and at higher temperatures forms other complex organic compounds. For this reason, it is essential that ample water should be present to absorb the heat of the reaction or other means must be provided to prevent an excessive rise in temperature. Experiments on the temperatures occurring in generators have shown a maximum of from 280° up to as high as 807° C. Furthermore, at high temperatures, the acetylene may decompose violently, the critical point being about 780° C. The heat set free may thus result in an explosion, while if any air is present, it may explode at 480° C. On account of these facts it is exceedingly important that well-designed generators should be used for the production of the gas. The generators may be divided into two general classes: first, where the carbide is added to the water, second, where the water is added to the carbide. Either of these may be automatic or non-automatic. The Ameri-

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[6] See Chapter 12.

can regulations require that the maximum rise shall not exceed 53° C., and that there shall be present at least 8¼ lbs. of water per pound of carbide, while for the hand-fed generators the rise shall not be over 91° C.

Owing to the rise of temperature in the generator, considerable water is vaporized and passes off with the gas, so that a generator requires considerably more water than is indicated by the reaction, the usual allowance being about half a gallon per pound of carbide.

Properties of Acetylene. Pure acetylene has a sp. gr. of .9056; its critical temperature is 37° C. and the critical pressure 68 atmospheres. The specific heat is .373 and its calorific value is 1440 B.T.U. per cubic foot. When mixed with air, it ignites at about 430° C. Its explosive limit varies from about 2.5 to 55 per cent.

At 15° C. it is soluble, volume for volume, in pure water, but the presence of lime or sodium salts in the water such as would exist in the generator reduces the solubility to about one-third of this figure. Above two atmospheres' pressure and at 780° C., acetylene is very unstable and is likely to decompose violently. For this reason liquefied acetylene is very dangerous and its use is generally prohibited. Various solvents such as acetone will take up large volumes of acetylene and this property is made use of in portable tanks. The tanks are filled with a porous material, containing about 80 per cent of voids; about 43 per cent of these are filled with acetone. The acetylene is then compressed into the cylinder at a pressure of 10 atmospheres, at which pressure the cylinder will hold about one hundred times its volume of acetylene.

Crude acetylene, when first generated from the carbide, contains traces of ammonia, hydrogen sulfide and phosphine; these impurities are removed by scrubbing with water and a solution of caustic soda.

Generators—Figure 13 illustrates one type of automatic acetylene generator as used to produce acetylene under sufficient pressure for use in cutting torches.

Where the acetylene is produced in a central plant and compressed in cylinders, the generators are usually somewhat larger. They are rated according to the charge of calcium carbide contained in the magazine. Generators of about 350 lbs. are frequently used. In such generators the carbide feed is controlled by a small electric motor or water motor which operates in connection with the diaphragm so that the pressure in the generator is maintained between 6 and 8 lbs. On a large scale, the gas passes from the generator through a water scrubber and then into a small gas holder of 10,000 to 20,000 cu. ft. capacity.

Use of Cylinders. In commercial production of acetylene, the gas is sold in steel containers filled with asbestos discs saturated with acetone. The asbestos discs have a porosity of between 75 and 80 per cent. About 40 per cent of this pore space is filled with acetone. Acetone will dissolve about twenty-five times its volume of acetylene at atmospheric pressure and the Interstate Commerce regulations permit a pressure of 250 lbs.

The cylinders are about 12 in. in diameter and 36 in. high. They are usually seamless-drawn bodies with a welded end. They must conform to I.C.C. specifications No. 8. The thickness is about 1.75 in. and the steel is about .16 per cent carbon, .02 per cent phosphorus, .04 per cent sulfur, with an elastic limit of 45,000 lbs., 55,000 to 60,000 lbs. tensile strength, 22 to 28 per cent elongation. The cylinders are tested at 750 lbs. pressure for temporary and permanent deformation. The permanent deformation must not be over 10 per cent, the temporary deformation at this pressure. The cylinders are also tested at 500 lbs. for leakage.

As mentioned before, the cylinders are filled with asbestos discs that are saturated with acetone. The amount of acetone used per cylinder must be kept at a fixed amount, as its weight must be included in the weight of the cylinder to determine the capacity of the cylinder, since the volume is determined from the increase in weight of the cylinder at the standard pressure and temperature.

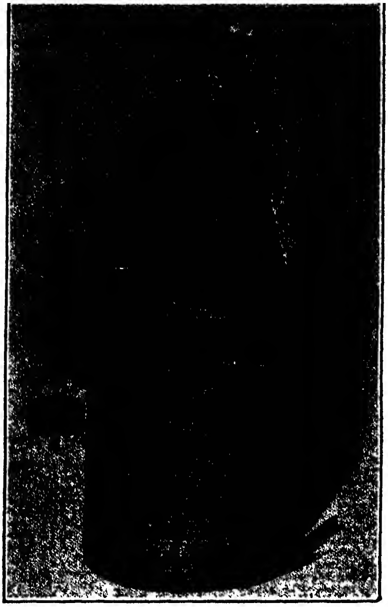

Fig. 13. Acetylene Generator.

The cylinders usually contain from 36 to 40 lbs. acetone and will hold from 250 to 300 cu. ft. at 250 lbs. The acetylene is usually calculated to be equivalent to 14½ cu. ft. per pound.

In filling the cylinders after they have been inspected and acetone added if necessary, the gas is then passed through a scrubber and dryer filled with lump sodium hydroxide and then through an oil separator. From the oil separator the gas passes into a manifold to which the charging cylinders are connected by thin metallic piping. While the gas is being admitted, the cylinders are sprayed with water to keep them cool and when the pressure has reached 300 lbs., they are disconnected and laid on their side in order to equalize the gas throughout the cylinder and are usually allowed to remain overnight, during which time the pressure falls to 150 or 200 lbs. They are then connected again and the pressure brought up to 250 lbs. They are again disconnected, tested for leaks and weighed. After this, they are allowed to stand for at least two hours in order to distribute the gas throughout the cylinder.

OXYGEN

The great increase in the use of the oxy-acetylene torch for welding and cutting metals has given rise to an important industry, the manufacture of compressed oxygen. One of the most important instances has been its use in the manufacture of welded structural members to replace the heavy castings formerly used in the framework of many machine tools. This has resulted in a great saving in waste, and the ability to redistribute the metal so that greater rigidity is obtained. The development of all-welded steel ships and the welding of the structural framework of buildings has become a reality within recent years (Figure 14). Many other interesting developments have appeared, such as the use of torches of special design for removing the mill scale from ingots and all types of metallic structures previous to painting (Figure 15). Not only is the greater portion of the loosely adherent mill scale removed but what is left is dehydrated and, after brushing, is painted with a priming coat before the material has had an opportunity again to absorb moisture.

Another development that promises to be of considerable commercial importance is the local surface hardening of gears, shafts, etc., by rapid heating followed by suitable quenching. This has been applied to gear teeth, lathes, guides, and spindles where a local surface hardening is very rapidly obtained. Figure 16 shows an interesting application.

An outgrowth of the welding technique has been the oxygen-cutting of steel on a very large scale (Figure 17).

As a result of these new developments and with a very large extension of the use of gas welding, the production of oxygen has increased very rapidly and the last available figures indicate the production of about a billion cubic feet a year. This calls for an extensive distribution system and large-scale delivery methods. One method of distribution is to mount multiple tanks of compressed oxygen on a trailer which is hauled directly to the job and left there. When the trailer-tank supply is depleted, another trailer is hauled in, the original trailer returning to the plant for recharging.

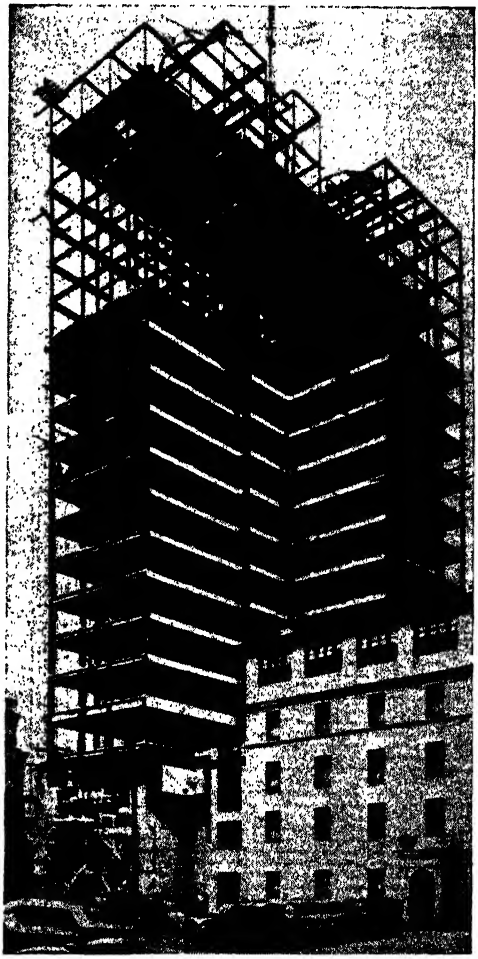

FIG. 14. All-welded Building. (Courtesy Air Reduction Sales Co.)

Formerly, the small amount of oxygen that was used with the oxy-hydrogen blowpipe in the platinum industry and in projection apparatus was manufactured by chemical methods. On a very small scale, the laboratory method of decomposing potassium chlorate in the presence of manganese dioxide was used, while in the larger plants the barium peroxide (Brinn) process was employed. This process depends upon the fact that barium peroxide will give off oxygen at a relatively high temperature under partial vacuum and will absorb oxygen from the air when a moderate pressure is applied.

Oxygen is also a by-product in the electrolytic production of hydrogen which was discussed above.

Liquid Air Process—The great development in the manufacture of commercial oxygen came with the introduction of the liquefaction process whereby oxygen is distilled from liquid air.

Fig. 15. Flame Cleaning and Dehydrating Steel Surface. (Courtesy Air Reduction Sales Co.)

The liquefaction product which had been a laboratory curiosity was made a commercial possibility by the work of Linde and Claude. Linde employed the principle of counter-current cooling to the Joule-Thompson effect to produce the low temperature necessary to liquefy the air. Claude cooled the air by expanding a portion of the air in an engine, thus producing the necessary drop in temperature. In whatever fashion the initial drop in temperature is secured, the cooled air is passed back through a heat exchanger, thus lowering the temperature of the incoming air, so that a progressive cooling takes place until the temperature is reached at which the air begins to liquefy. It was this self-cooling principle that made commercial liquefaction possible. After the air is liquefied, the oxygen is separated from the nitrogen by rectification in a bubble-cap column.

Power Requirement. The theoretical power required to separate air into its constituents, oxygen and nitrogen, is that necessary to compress isothermally the components from their respective partial pressures to atmospheric pressure. This amounts to slightly less than 3 H.P. per 1000 cu. ft. of oxygen per hour. Actually, however, due to the fact that the energy put into the air is not recovered, about 35 H.P. per 1000 cu. ft. of oxygen per hour is required. At the present time, due to the expiration of the early patents, there are a number of types of commercial apparatus in use. They are all fundamentally alike, the principal variations having to do with the design and arrangement of the heat exchangers and the details of the fractionating columns. The efficiency of the process is very largely dependent upon the operation of the heat exchangers.

FIG. 16. Flame Hardening Gear Teeth. (Courtesy Air Reduction Sales Co.)

In some of the earlier and simpler designs the heat exchangers consisted of bundles of thin-wall tubing that were brazed or bound together to secure good thermal contact. More recently, several types of deformed tubes have been used to increase the surface exposed and to secure better contact with the gases. In other forms, the space around the tube has been packed with metallic filling to secure better contact. The tubing is usually made of copper and the joints soldered to insure strength and tightness.

There has been some development in the use of metallic regenerators instead of the usual form of heat exchanger. These regenerators are of very simple design, made of coils of thin sheet metal. They are used in a manner similar to the regenerative stoves in a blast furnace. It is claimed that their simple construction and low cost together with their high efficiency result in a considerable decrease in the production cost of the oxygen.

Fractionation. The fractionating column itself is quite similar in design and operates in precisely the same manner as the fractionating columns used in the distillation of coal-tar light oils and alchol, which have been described elsewhere in this book.

If we disregard traces of rarer gases, we have in liquid air a simple two-component mixture which boils at 81° K., the oxygen boiling at 90.5° K., the nitrogen at 77.5° K., so that we have a difference of some 23° between the boiling point of the two constituents which is sufficient to give reasonably good separation of one component. The heat necessary to boil the liquid at the bottom of the still is furnished by the incoming air that is passed through the heat exchanger prior to its passage through the expansion chamber. The air is liquefied at the top of the fractionating column and as it passes down through the sections in the column, the nitrogen boils off while the liquid oxygen flows down and collects in the bottom of the still.

Fig. 17. Multiple Torch-cutting of Steel Plates. (Courtesy Air Reduction Sales Co.)

General Operation. Dry purified air at a pressure of from 60 to 200 atmospheres enters the column through the pipes and is cooled in passing through the heat exchanger and the heating coil in the base of the still. This partially-cooled air then rises through a pipe to the expansion valve where the air is expanded to about 6 lbs. per square inch. When the column is first started it is necessary to have the pressure at approximately 200 atmospheres. As the column cools down and the air begins to liquefy, it is possible to reduce the pressure to about 50 atmospheres. The cooling due to the Joule-Thompson effect lowers the temperature to a point where the air is liquefied. The liquefied air drains down through the plates in the column. The nitrogen boils off so that as the liquefied gas passes down through the column, it becomes progressively richer in oxygen and poorer in nitrogen so that at the base of the column the liquid is practically pure oxygen. The heat head necessary to operate the column is furnished by the incoming air which is passed through the coil. This boils off a sufficient amount of oxygen to furnish the vapors necessary for the fractionation. The nitrogen together with some of the oxygen passes up out of the column through the heat exchanger and passes out at the top of the column through a pressure regulator valve and is discharged to the atmosphere.

The still is operated with sufficient pressure to force the liquid oxygen up through the heat exchanger where it is vaporized, thus cooling the incoming air, the oxygen passing out through a pipe to the meter and holder. The column is very heavily lagged with non-conducting material and is provided with gauges indicating the pressure at the various points which are necessary to determine when the small traces of moisture and carbon dioxide which have escaped the purifying system have accumulated to such a point that the column ceases to operate properly. When this occurs, it is necessary to "defrost the column"; that is, melt out the ice or solid carbon dioxide collected. This is usually done by passing nitrogen back through the column. With good operation, defrosting is not required more than once a week, when it will require from four to six hours shutdown after which the manufacture of oxygen can again begin in about two hours. Where the column is merely shut down, it will deliver oxygen in from one-half hour to forty-five minutes after starting.

Purification of Air. The carbon dioxide and water vapor must be removed from the air before it reaches the fractionating column, as both of these would solidify at the operating temperatures and would quickly clog the column. The carbon dioxide is removed by scrubbing the air in two towers with a solution of caustic potash. These towers are packed with iron rings to increase the surface, and the caustic potash solution passes down these columns against the rising current of air.

Two strengths of caustic potash solution are used in scrubbing the gas. The solution is made up very strong originally. This is used in the second tower and when its strength has fallen, it is used in the first tower. After it has been exhausted in this tower, it is discarded. These purifying towers are provided with separators at the top to prevent any of the spray in passing over with the air. The air freed from carbon dioxide is then passed to the compressor.

Compressors. Since the greater portion of the energy required is utilized in compressing the air, it is essential that the design of the compressor should be such as to give efficient and dependable results. The compressors are usually four-stage and are electrically driven. Piston rings are used instead of stuffing boxes. The cylinders are arranged with No. 2 and No. 4 on the outside with No. 1 and No. 3 between, in order to prevent leakage of unpurified air into the low-pressure cylinder. The valves are usually of the automatic type and lubrication is taken care of by means of a four-speed cycle that uses a high-flash oil.

Although the pressure required to start the system may approximate 200 atmospheres or about 3000 lbs. per square inch, the operating pressures are much lower and are usually 50 atmospheres or about 750 lbs. per square inch, the pressures developed in the cylinders in normal operation are about 30-150-550 and 750 lbs. per square inch. In order to remove the large amount of heat developed during the compression very efficient inner-coolers are provided between each stage.

The cooler between the first and second stages is usually of the condenser type and is mounted directly over the cylinder, while the other coolers are usually of the pipe-coil type mounted in a water tank at the high-pressure end of the compressor. During the compression, some water vapor and oil collects in the coolers and is blown off at intervals. From the compressor, the high-pressure air is passed through a separator consisting of a steel cylinder to act as an oil drip and three steel cylinders arranged in series, containing lumps of caustic potash. These high-pressure purifiers are provided in duplicate. Each cylinder will hold about 160 lbs. of lump caustic. The lump caustic not only removes the last traces of carbon dioxide but also removes traces of water vapor.

From the caustic drying cylinders the air is passed through a small trap to remove caustic dust which might be carried over and from here it will pass through the fractionating column, for a plant having a capacity of 25,000 ft. per day. The column itself is about 10 ft. high and 12 in. in diameter. It is enclosed in an insulated jacket about 12 ft. high and 3 ft. in diameter. The heat exchanger is in the upper part of the column, and the fractionating plates in the lower portion of the column; the expansion valve is at about the middle. The purified and compressed air enters at the top, passes through the heat exchanger where it is cooled by the outgoing products, then passes through a coil in the base of the still where it boils the liquid oxygen, then passes to the expansion valve and is liquefied. The pure liquid oxygen is collected in the base of the column and is afterwards passed to the heat exchanger where it is vaporized and thus assists the incoming air, and passes out of the column from the top of the heat exchanger. The nitrogen, which contains about 10 per cent of oxygen, passes out of the column through the heat exchanger. The operation of the column is controlled to a considerable extent by the back pressure in the column, which is regulated by a valve in the nitrogen line.

The column is naturally operated so as to produce oxygen of a suitable purity. This is usually 99.2 and 99.5 per cent and is determined by absorbing the oxygen in a gas pipette filled with copper wire in a solution of cuprous ammonium chloride or carbonate. By increasing the back pressure in the column the yield of oxygen is cut down and the purity is increased. The liquid oxygen is passed from the column through a meter and on to the storage holder. The cylinders used in distributing compressed oxygen are made to meet the I.C.C. regulations 3A. These cylinders are of seamless steel and are tested to 3600 lbs. The cylinders are manufactured so that they will contain around 110 or 220 cu. ft. measured at 2000 lbs. pressure and 70° F. temperature. The oxygen is usually compressed with a three-stage compressor of the same general type as that used in the main compressor. For lubrication, a weak solution of soap and water is used.

MISCELLANEOUS GASES

Pintsch Gas—Pintsch gas is a compressed oil gas of high illuminating value and was used almost exclusively for lighting railway cars and to some extent for buoys. The use of electricity for car lighting and the development of propane and butane have resulted in the practical abandonment of manufactured Pintsch gas and other gases manufactured from petroleum, such as Blau gas and Dayton gas, that at one time found some application as industrial gases.

Other Gases from Petroleum—One of the most rapidly expanding fields of chemical industry is found in the synthesis of materials from gases derived from petroleum. Synthetic rubber, a variety of plastics, aviation gasoline, solvents, and a great array of organic chemicals are now based on the use of the parent substance, petroleum. A number of these applications are treated elsewhere.[7]

FURNACE ATMOSPHERES

The various industrial gases heretofore discussed have been combustible and were used primarily as a source of heat energy. There exists, however, an important industrial use for generally non-combustible gaseous mixtures which are used to form the atmosphere surrounding the work during a variety of heat-treating operations. Such operations would include the atmospheres used in annealing, carburizing, drawing, forging, and hardening steel; in the annealing of copper, brass, nickel and other non-ferrous metals; and in the annealing and forming of glass. Other industrial processes such as japanning and vitreous enameling use similar atmospheres. A further use is in the prevention of combustion or explosion in the handling of readily combustible materials frequently existing in the dust form, and in the manufacture of varnish.

Action of Gases—The action of these controlled atmospheres will depend upon the particular process and will vary from (1) a simple blanketing effect, to prevent the access of atmospheric oxygen to an active part in the process, by furnishing a controlled amount of oxygen, to (2) a small amount of reducing action by the presence of carbon monoxide and hydrogen, or (3) to furnish an excess of carbon-bearing components to add carbon to various materials. The nature of the atmosphere is generally described as oxidizing, neutral, or reducing and these terms have been defined by the American Gas Association as follows:

TABLE 8—AMERICAN GAS ASSOCIATION DEFINITIONS OF FURNACE ATMOSPHERES

Type	*Sum of Hydrogen and Carbon Monoxide*	*Oxygen*
Oxidizing	less than 0.05%	more than 0.05%
Neutral	less than 0.05%	less than 0.05%
Reducing	more than 0.05%	less than 0.05%

These definitions only characterize the type of atmosphere and are not of much service in determining the composition required for any particular prob-

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[7] See Chapter 14.

lem, since in many cases the effect of the presence of water vapor, carbon dioxide and sulfur compounds may be controlling factors.

Production of Furnace Atmospheres—These atmospheres are usually created by burning a combustible gas mixture, using an adjusted air-gas ratio so that the oxygen may be more or less completely removed during the combustion, leaving various amounts of hydrogen, carbon monoxide and carbon dioxide whose relative occurrence will depend upon the fuel and the particular air-gas ratio used. Another general method is to decompose the fuel gas in a heated muffle.

In the first method the gas is burned with a controlled air supply in a tube or muffle which is usually provided with means for controlling the temperature and is frequently provided with an auxiliary chamber containing a catalyst. The products of the combustion are cooled and then washed with various reagents, depending upon the requirements, to remove carbon dioxide and sulfur compounds and in many cases the water vapor is removed by refrigeration or by treatment with activated alumina or silica gel.

City gas, natural gas, and compressed petroleum gas have all been used as a fuel gas and the composition of the final mixture can be varied over a wide range to suit the special requirements of the process. It is difficult in any of these combustion methods to reduce the oxygen below 0.05 per cent and it is still more difficult to determine it accurately at these low concentrations.

In the second method the muffle or retort is externally heated and the gas to be decomposed is passed through it. At the present time this process is used almost exclusively for the decomposition of ammonia, forming hydrogen and nitrogen. The hydrogen can be adjusted by combustion with air to any desired extent.

Controlling the Atmosphere—In treating ferrous metals the temperature is an important factor in determining the composition of the atmosphere that may be used. Generally, carbon dioxide and water vapor are deleterious constituents and are removed. In the annealing of non-ferrous metals such as copper and brass, the presence of sulfur compounds must be avoided as far as possible. Concentrations of hydrogen sulfide as low as 0.01 grains per 100 cubic feet may give trouble. There is some evidence to indicate that the presence of the nichrome heating elements in electric furnaces may cause the formation of hydrogen sulfide from sulfur compounds which would otherwise not be injurious. Table 9 gives the analyses of some atmospheres that have been used with certain types of heat treatment.

TABLE 9—COMPOSITION OF SOME COMMERCIALLY USED ATMOSPHERES

Use	*Carburizing*	*Annealing Strip Steel*	*Bright Annealing Copper and Brass*	*Hardening Springs*
CO	15	8.7	1.8	11.2
H_2	18	9.6	1.4	14.0
CH_4	8	1.9	....	....
CO_2	2	5.8	13.0	4.6
H_2O Dew Point	......	below 30° F.	below 40° F.	....

The gas industry itself makes use of a controlled atmosphere produced by the complete combustion of gas with air to form an inert, practically neutral atmosphere which is used in purging purifiers, storage holders, mains or any apparatus that has been used to contain gas, in order to prevent the development of explosive mixtures.

SECTION IV

REFRACTORIES AND ALLIED MATERIALS

This section deals with those oxidized materials of construction which undergo sufficient processing to be classed with the chemical industry. Because they are maintained in their completely oxidized state, their chief characteristic is resistance to atmospheric corrosion. This type of material has played a prominent part in human affairs for thousands of years and will undoubtedly always have an important place in our industry.

CHAPTER 20

GLASS

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HISTORICAL

The farther back the archeologist pushes the curtains of history the farther back go the beginnings of glass manufacture, and it is probable that man has known how to make glass ever since the earliest beginnings of civilization. Glass was made in quantity by the ancient Egyptians, and during the Golden Age of Egypt, the Eighteenth Dynasty (about 1500 B.C.), glass manufacture was a well-established industry, and some of its products were of excellent quality. Glass artifacts have been described from Egypt apparently dating from much earlier periods, but there is difference in opinion among experts both as to their proper identification as glass and as to their dating. It is probable that we must look to Asia Minor for the beginnings of the industry. Beads of glass were plentiful in a cemetery at Ur, dating to 2450 B.C., and possibly the oldest piece of glass ever discovered was found at Tel Asram, a few miles northeast of Bagdad, dating to 2900 B.C. Sculptural records of the Eighteenth Dynasty show Syrian workmen being brought into Egypt, carrying with them vases of glass or metal which they had manufactured. The Syrians probably were far ahead of the Egyptians up to this period in art and industry, and it is believed that the glassware imported into Egypt prior to this period was of Syrian origin.

The presence of a stable domestic glass industry at the beginning of the Eighteenth Dynasty is shown by remains of glassworks of that period, which are still to be seen. It has been stated that the end of this Dynasty corresponded to the best period in Egyptian art, especially in glass; and Egyptian glass of 1400 B.C. was more durable, and required more technical skill in its manufacture, than that of some later periods. From this time until the beginning of the Christian Era, Egypt remained the chief center of glass manufacture, and its glassware was distributed throughout the world. The industry became centralized in Alexandria, from which place under the stimulus of the Ptolomaic revival, it was carried to Syria, Greece, Palestine, and Italy. For data on the composition of some of these ancient glasses, see Table 1.

Before the invention of glass-blowing, glass was used chiefly for jewelry, especially beads, and for small hollow ware such as unguent jars and small vessels which were not blown but molded. The process was laborious and of limited scope and was merely a core of sand built up on a wooden or metal rod and then covered with glass by building up with viscous glass not much above its softening temperature. Later, probably about 1200 B.C., another technique was developed, that of pressing the glass into open molds. By this means shapes such as bowls, dishes, and cups, which could not be made by the sand-core process, were added to the repertory of types which were at the disposal of the glass-maker. Transparent glass was rare, the quality of transparency not being important for the use for which the glass was intended.

Glass-Blowing—The invention of glass-blowing caused an industrial revolution which changed a luxury into a necessity. Glass had been used only for small and precious articles, but the process of shaping glass with the aid of the blow-pipe made possible the production in quantity of a better and cheaper article. The time and place of the first free glass-blowing are not certain but it probably took place a little before the beginning of the Christian Era. The rapid expansion of the industry which followed was due in part to the invention of glass-blowing but it could not have taken place but for the commercial stability afforded by the Roman Empire.

There is little information concerning glass manufacture in the period following the fall of the Roman Empire until the rise of the Venetian glass industry in the eleventh century. During this period glass manufacture was actively developed in the Eastern Empire and the Byzantine workers were especially adept in making colored glass and mosaics. Probably as an indirect result of the Crusades and of the fall of the Eastern Empire, glass manufacture in Venice entered into a period of development about the beginning of the eleventh century which soon made that city the center of the glass industry. This position it held for at least four centuries. From Venice the art spread throughout Western Europe, and its development became rapid. In 1600 the art of making cut glass was developed and in 1615 the use of coal instead of wood for fuel was discovered in England.

Another English invention, the use of lead oxide to produce "flint" glass, was made in 1675. Faraday's researches on glass are a classic of the early part of the nineteenth century, and the work of Schott, associated with Abbe and Winkelmann, inaugurated a new period in the science of glass.

This century has seen the transformation of the industry by the invention of machine processes for forming glassware. The beginnings of this movement were made in the previous century, but its active progress was begun by the invention of the first commercial bottle machine by Owens in 1904 and since then the development of machine processes has been rapid. The first significant advance in glass composition was the development of the low expansion Pyrex chemical resistant glass. Subsequent developments have given us a clear understanding of the basic scientific principles underlying the manufacture of glass, which now are being intensively applied by several companies.

DEFINITION AND STRUCTURE OF GLASS

Glass is an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of that substance but which has attained so high a degree of viscosity as a result of having been cooled from the fused condition that it is, for all practical purposes, rigid. All known glasses are thus undercooled liquids.

This definition excludes all organic substances. Some organic materials such as glucose solutions and certain plastics[1] would otherwise be included in the glasses but since they differ so greatly in composition, methods of manufacture, and properties from the substances which have always been known as glass, they are classified in a different division of chemical technology.

Transparency is frequently considered a characteristic of glass, yet much commercial glassware is either translucent or opaque. It is always true, however, that the lack of transparency is caused by the fact that some material, usually crystalline, is dispersed or suspended in a glassy matrix which is itself transparent. The material may be a colloidal suspension, as in a gold or copper ruby glass; or a suspension of submicroscopic to microscopic particles, as in some opaque glasses; or microscopic crystals ranging in size from the lower limits of resolving power to fairly coarse crystals, as in some opals and white glasses. In all of these cases, however, the material is essentially glassy.

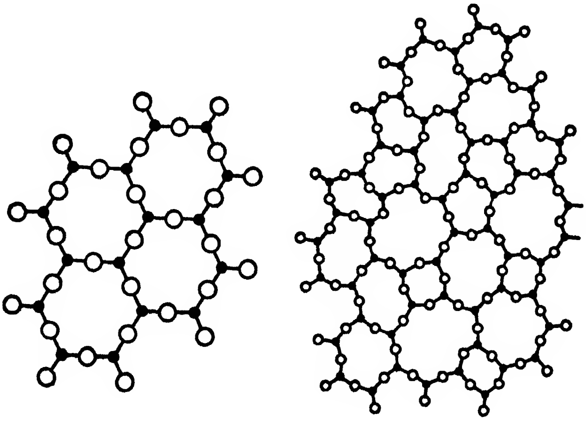

FIG. 1. Schematic Representation in Two Dimensions of the Difference Between the Structure of a Crystal (*left*) and a Glass (*right*). (After Zachariasen)

The dominant characteristic of glass is that it is a rigid material obtained by cooling from the fused condition, with resultant continuously increasing viscosity, but without crystallization. The definition has been so worded as to exclude the necessity of its being below its proper freezing point, that is, an undercooled liquid. The circumstance that all known glasses are undercooled liquids is not, so far as we know, essential. A material might have its true freezing point below ordinary temperatures and yet be rigid enough for use as glass, and be properly considered a glass. However, no such material is known.

The essential feature is that glass has the non-periodic structure of a liquid,[2] and X-ray studies have shown that the atoms in glass form a network which is not periodic and symmetrical as in crystals. In silica crystals the dominant feature is the tendency of each silicon to be tetrahedrally surrounded by four oxygen atoms and each oxygen bonded to two silicons. The orientation of each tetrahedral group to every other is definitely fixed and indefinitely repeated in

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[1] See Chapter 31.

[2] Zachariasen, W. H., J. Am. Chem. Soc. *54*, 3841 (1932).

space. In silica glass[3] the dominant feature is still the tendency of each silicon to be tetrahedrally surrounded by four oxygen atoms, but the orientation of any one tetrahedral group with respect to neighboring groups can be practically random. The difference in structure between a crystal and a glass is illustrated in Figure 1. In silicate glasses the same tendency toward tetrahedral grouping persists. As other oxides are introduced and the number of oxygen atoms to each silicon atom is increased, some oxygen atoms become bonded to only one silicon. Figure 2 shows a schematic two-dimensional representation of the structure of soda-silica glasses[4] in which each silicon is shown surrounded by only three oxygens instead of four as in a spatial representation. Some of the oxygens are bonded to two silicons, others to only one silicon, and as the SiO_2 content is decreased with increase in M_2O and MO the proportion of singly-bonded oxygens increases. The sodium ions occupy holes in the irregular silicon-oxygen networks and in soda-lime-silica glasses the calcium ions occupy similar positions.

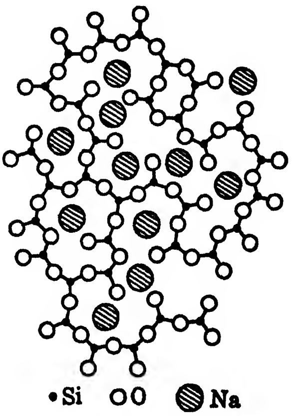

FIG. 2. Schematic Representation in Two Dimensions of the Structure of Soda-silica Glass. (After Warren and Biscoe)

COMPOSITION OF GLASS

Commercial glassware is for the most part of simple composition. It is a soda-lime-silica glass containing relatively minor quantities of magnesia, alumina, and sometimes boric oxide. This relatively simple composition is essentially that which has been used for glass from the earliest times, and the reason for this narrow range in composition is the basis of glass technology.

The essential feature of glass is that when it is cooled from the molten condition it does not devitrify or crystallize. Molten glass resembles other molten substances in that on cooling it has a true freezing temperature at which crystals should begin to separate. This is the same as the melting temperature, where the last trace of crystals will dissolve in the melt. However, glass differs from other materials in the readiness with which it undercools, that is, passes through its freezing point without freezing. The temperature at which glass is melted bears no relation to its true melting or freezing point which is called the liquidus temperature.

Devitrification ruins the glass, and the composition must be so adjusted that the glass does not crystallize, especially during the shaping and annealing processes. The two features which are of importance are first, the actual liquidus temperature above which the glass cannot devitrify because it is above its melting point, and below which it will crystallize under certain conditions, and second, the viscosity. All commercial glass compositions are melted at temperatures higher than their liquidus temperatures, but most glasses are subjected to shaping operations at temperatures near to and frequently below their true freezing points.

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[3] Warren, B. E., Z. Krist. *86*, 349 (1933).

[4] Warren, B. E. and Biscoe, J. J., J. Am. Chem. Soc. *21* (7), 259 (1938).

Hence at shaping temperatures the viscosity must be great enough to prevent crystallization under ordinary conditions of working. The change of liquidus temperature with composition requires more detailed discussion.

Phase Equilibrium—The phase equilibrium diagram[5] of the system Na_2SiO_3—$CaSiO_3$—SiO_2 is given in Figures 3 and 4. The diagram is divided into a number of fields, in each of which a different compound is the first to crystallize on cooling. In Figure 3 the fields are separated by heavy lines and isotherms (lines of equal liquidus temperature) are shown. In Figure 4 the isotherms are omitted and the compositions of the primary phases are indicated. A region of immiscibility extending in the binary system CaO—SiO_2 from 72.5 to 99.4 per cent SiO_2 is not shown on the ternary diagram because a small quantity of Na_2O removes this immiscibility. In Figure 4 the arrows on the boundary curves indicate the direction of falling temperatures.

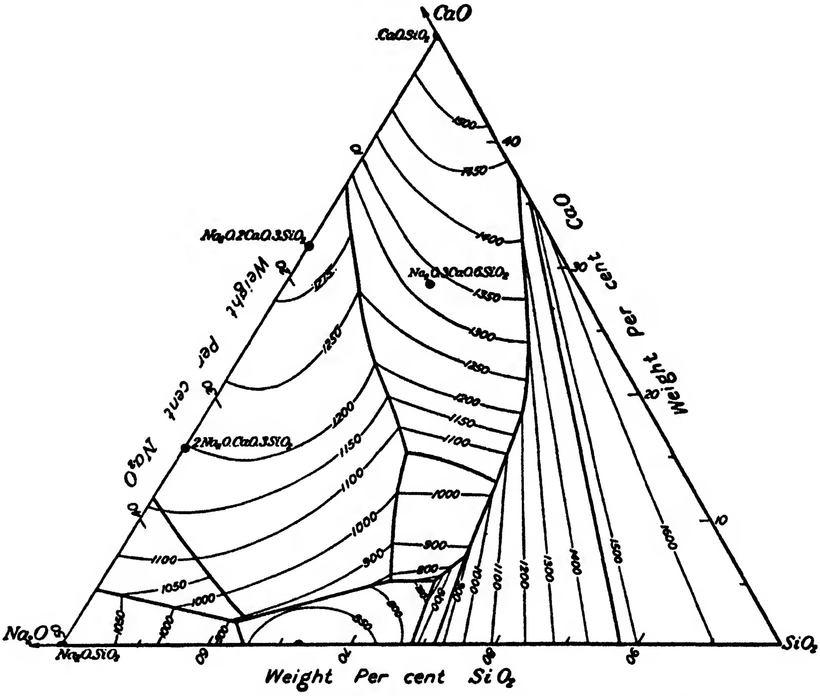

Fig. 3. Phase Equilibrium Diagram of the Ternary System Na_2O-CaO-SiO_2, Showing Isotherms. (After Morey and Bowen)

The three forms of silica, cristobalite, tridymite and quartz, occupy the SiO_2 corner of the diagram. The field of cristobalite is above 1470° C., and any mixture in this field crystallizes readily, and the compositions are too viscous even at high temperatures for glass manufacture. Mixtures in the high temperature part of the tridymite field are also viscous and crystallize readily, but the lower part

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[5] For references on the principles of phase diagrams see reading list at end of chapter.

of the field, especially below 1000° C., represents a field of useful glass compositions.

Water Glass—The side of the diagram sodium metasilicate—silica contains the compound sodium disilicate. No mixtures on this side-line are suitable for commercial glass compositions because they are easily decomposed by water but they form the basis for the industry of soluble silicates, the water glasses of commerce. Most soluble silicate is made with a ratio of Na_2O:SiO of about 1:3.2, but silicates are made in which this ratio ranges from 2:1 to 1:3.9. The soluble silicate industry in 1939 produced 655,379 tons of liquid of 40° Baumé, valued at $7,298,463, and 46,012 tons of anhydrous glass, valued at $1,799,082.

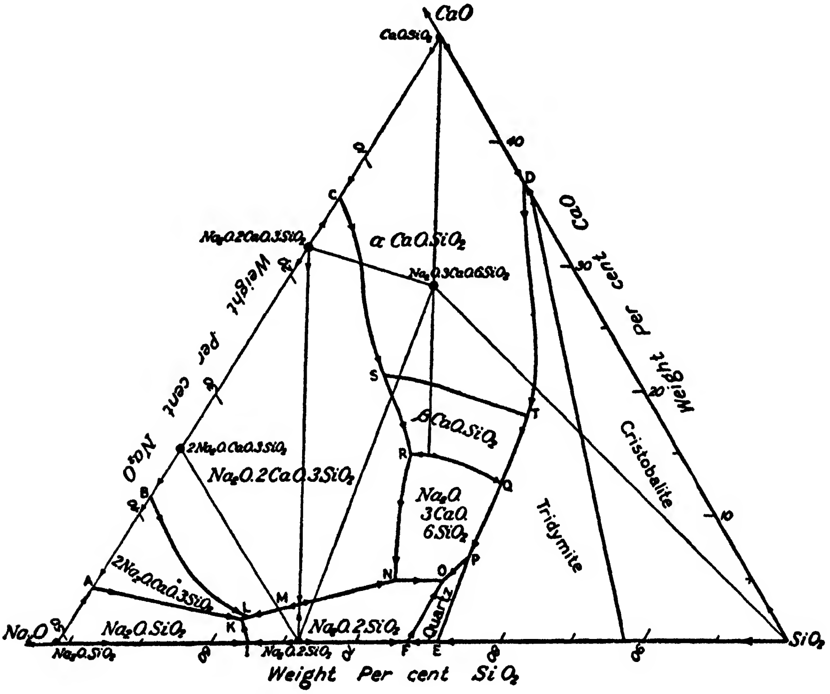

FIG. 4. Phase Equilibrium Diagram of the Ternary System Na_2O-CaO-SiO_2, Showing Boundary Curves and Tie-lines. (After Morey and Bowen)

Glass of the composition of sodium metasilicate, Na_2SiO_3, can be obtained only in small quantity, but glasses from which sodium disilicate, $Na_2Si_2O_5$, is the primary phase are easily manufactured in large quantity. A glass of the composition of the eutectic between sodium disilicate and quartz is very difficult to crystallize. Except for the lack of chemical durability it would be an excellent composition, so that something must be added to increase its resistance to attack by water. The substance added is usually calcium oxide because it gives an excellent product and is itself cheap.

The side of the diagram which represents the binary system Na_2SiO_3—$CaSiO_3$ contains two ternary compounds. The field of one of these, $2Na_2O \cdot CaO \cdot 3SiO_2$, does not extend over the composition of the compound and the compound is said to melt incongruently. Compositions in which it occurs are too readily decomposed by water to be of value for glasses. The other compound, $Na_2O \cdot 2CaO \cdot 3SiO_2$, has a large field which extends to a silica content of 70.7 per cent at the reaction point

$$Na_2O \cdot 2SiO_2 + Na_2O \cdot 3CaO \cdot 6SiO_2 = Na_2O \cdot 2CaO \cdot 3SiO_2 + \text{liquid}$$

Some glasses have been found to lie in this field, but they are of inferior durability and crystallization takes place readily.

$CaSiO_3$ occurs in two forms. The mineral wollastonite changes at 1100° C. into a high-temperature form called pseudo-wollastonite. The field of the two forms is a ridge extending downward from $CaSiO_3$ and its eutectics with $Na_2O \cdot 2CaO \cdot 3SiO_2$ on the one hand and tridymite on the other, down to its boundary with the compound $Na_2O \cdot 3CaO \cdot 6SiO_2$. The mixtures richer in lime are high-melting and crystallize readily. It is only in the lower corner of its field adjacent to the field of tridymite that the melting point is low enough and viscosity great enough to be used.

The compound $Na_2O \cdot 3CaO \cdot 6SiO_2$ has been named "devitrite" because it is the crystalline compound which is formed in the devitrification of a large number of commercial glasses. Its field is surrounded by the several fields which have been discussed, and it extends down to the lowest temperature in the system, the ternary eutectic

$$Na_2O \cdot 2SiO_2 + Na_2O \cdot 3CaO \cdot 6SiO_2 + SiO_2\ (\text{quartz}) = \text{liquid}$$

at 725°. All mixtures in this field are possible glass compositions, although those adjacent to the fields of $Na_2O \cdot 2SiO_2$ and $Na_2O \cdot 3CaO \cdot 6SiO_2$ are of poor chemical durability. The Corning "015" glass widely used for glass electrodes is near the composition of the ternary eutectic.

The Soda-Lime Glasses—Most successful glass compositions are in the field of devitrite, usually in the silica-rich portion of the field, and sometimes a little over the boundary in the tridymite field. The SiO_2 content ranges from about 69 to 72 per cent; CaO, from 12.5 to 13.5; Al_2O_3, from 1 to 4; and Na_2O, from 13 to 15. This general composition range has been used from the beginnings of glass manufacture and is used today because it includes the only compositions of matter which are fluid enough at an industrially accessible temperature to be melted on a commercial scale, viscous enough to be worked above their freezing points, and so viscous at their freezing points that they cannot devitrify.

Further discussion will deal chiefly with modifications of this fundamental glass composition. Pure soda-lime glasses are rarely used. Small amounts of other components are always present, either accidentally as impurities or deliberately added for modification of properties. Some or all of the limestone is frequently dolomitic, especially in this country, and the resulting glass is more difficult to devitrify than that containing CaO alone. However, a pure MgO glass is not satisfactory. Barium oxide is often added in small amount to make an easier-melting and more brilliant glass. Sodium oxide is frequently replaced by potassium oxide, especially in optical glasses, because of greater brilliance, and glasses containing both sodium and potassium oxides are superior in chemical durability. The use of potassium oxide is limited by its greater cost and the higher viscosity of the potash glasses.

Alumina in small amounts is practically always present, and amounts up to 2 or 3 per cent are common. It improves chemical durability and decreases the tendency to devitrify. The amount which can profitably be added is limited by the great increase in viscosity with resulting higher melting temperature and greater attack on refractories. Boric oxide is frequently added to make the glass easier to melt, to lower the coefficient of expansion, to improve chemical durability, and to decrease the tendency to devitrify. Iron oxide is usually kept at a minimum because of its objectionable color. However, in cases where the color does not matter, better chemical durability, freedom from devitrification, and ease of melting make it a desirable constituent.

Minor Constituents—Minor constituents of glass are either accidental impurities or substances added to secure some desirable effect. Iron oxide is usually present as an impurity which is undesirable because of its color. Several oxides, Cr_2O_3, V_2O_5, CuO, U_2O_5, MnO, NiO, CoO, are added as coloring agents. The chemistry of colored glasses is complex, and no comprehensive and adequate treatment has yet been published. As_2O_3 is often present as a "fining agent," a substance which aids in the removal of bubbles from the glass. Sb_2O_3 is sometimes present for the same purpose and is used in quantity in some optical glasses. NaCl and Na_2SO_4 are also used as fining agents. Sometimes much of the Na_2O is added as sulfate, in which case it melts and floats as an immiscible liquid and carbon must be added to reduce it. Fluorides and phosphates are used for opal glasses. Colloidally dispersed gold and copper are used in ruby glass, although most of the ruby today is a selenium ruby, in which the color is due to dispersed solid solutions of cadmium sulfide and cadmium selenide.

Glass also contains small amounts of volatile constituents, evolved on heating in vacuo, in such amounts as to give a volume of gas about the same as that of the glass. One gram of glass thus contains from 0.5 to 1.5 cc. of gas. The chief constituent is usually water, followed by carbon dioxide, nitrogen and oxygen. When sulfates are used in the batch SO_2 is usually found in quantities comparable to, or even in excess of the water.

Composition of Typical Glasses—The compositions of a number of glasses are given in Table 1. Numbers 1 to 4 are antique glasses. Neither of the glasses made in 1400 B.C. would be considered sufficiently weather-resistant for use today because of their high alkali content which was necessary to give a glass soft enough for easy working with crude furnaces. The glasses of the second and ninth centuries are similar to these glasses.

Prior to the development of glass-working machines glasses of much the same composition were used for most purposes. Representative compositions are No. 5, a window glass made by the old hand cylinder process, and No. 6, a bottle glass. Polished plate glass is high in lime, as shown by No. 7. Modern flat-drawn sheet glass is usually a little lower in CaO and contains some MgO, as shown in No. 8.

Modern high-speed machine production of container ware requires a glass not only of controlled viscosity but also having a definite viscosity-temperature curve, and this requirement has caused the development of special glass compositions. They differ from the older glasses chiefly in a reduction in CaO and an increase in the Na_2O and Al_2O_3 contents. A typical container glass is No. 9

TABLE 1—COMPOSITIONS OF SOME TYPICAL GLASSES

No.	SiO_2	B_2O_3	Na_2O	K_2O	MgO	CaO	BaO	ZnO	PbO	Al_2O_3	Fe_2O_3
1	61.70	...	17.63	1.58	5.14	10.05	...	...	...	2.45	0.72
2	62.71	...	20.26		4.52	9.16	...	...	...	1.47	0.96
3	69.82	...	13.51	2.18	3.09	5.79	...	...	...	1.40	1.80
4	68.48	...	14.95	2.83	5.28	5.71	...	...	...	0.70	...
5	72.26	...	14.01	...	...	13.34	...	...	...	1.42	
6	70.9	...	10.66	...	0.49	14.02	...	...	...	1.35	2.24
7	72.68	...	13.17	...	...	12.95	...	...	...	0.50	0.07
8	72.14	...	16.23	...	1.29	9.06	...	...	...	0.84	0.08
9	74.50	...	15.0	...	4.1	5.5	...	...	...	0.81	0.09
10	63.0	...	7.6	6.0	0.2	0.3	...	...	21.0	0.6	
11	73.6	...	17.23	...	3.67	5.37	...	...	...	...	...
12	75.9	...	7.1	7.9	0.17	8.7	...	...	...	0.14	0.08
13	64.7	10.9	7.5	0.37	0.21	0.63	...	10.9	...	4.2	0.25
14	80.5	12.9	3.8	0.4	...	...	...	...	...	2.2	...
15	74.6	...	9.0	11.0	...	5.0	...	...	...	...	...
16	70.4	7.4	5.3	14.5	...	2.0	...	...	...	...	...
17	40.6	...	1.5	7.8	...	...	...	...	43.8	...	...
18	28.4	...	...	2.5	...	...	...	...	69.0	...	...
19	34.5	...	...	...	...	...	42.0	7.8	...	5.0	...

1. Dark blue transparent fragment, 1400 B.C. Tell-el-Amarna. Neumann, B., Z. angew. Chem. *38*, 776 (1925); *41*, 203 (1928). Also contains: Mn_2O_3, 0.47; CuO, 0.32.
2. Light yellow translucent fragment, 1400 B.C. Neumann. Also contains SO_3, 0.92.
3. Assyrian-Babylonian glass, 250 B.C. Neumann. Also contains: Mn_2O_3, 0.41; CuO, 0.36; SO_3, 0.96.
4. Window fragment, Samarra, 9th century A.D. Neumann. Also contains: FeO, 0.91; PbO, 0.95; SO_3, 0.54.
5. Hand-made window. Sharp, D. E., J. Ind. Eng. Chem. *25*, No. 7, 755 (1933).
6. Hand-fed bottle. Sharp, No. 37. Also contains MnO, 0.30.
7. Polished plate. Sharp, No. 34. Also contains: SO_3, 0.44; Sb_2O_3, 0.18.
8. Fourcault sheet. Sharp, No. 17. Also contains: SO_3, 0.45; As_2O_3, trace.
9. Owens container. Sharp, No. 49.
10. Lead glass. Sharp, No. 55. Also contains: As_2O_3, 0.05; MnO, 0.2.
11. Lime bulb glass. Sharp, No. 62.
12. Kavalier beaker. Walker, P. H. and Smither, F. W., Tech. Paper No. 107, Nat. Bur. Standards (1918). Also contains: MnO, 0.02; P_2O_5, 0.08; SO_3, 0.20; As_2O_5, trace.
13. Jena Geräte beaker. Walker and Smither. Also contains: MnO, 0.01; As_2O_5, 0.14.
14. Pyrex chemical resistant glass. Morey, G. W., "Properties of Glass."
15. Crown, n_D 1.506 60.2. Morey.
16. Borosilicate crown, n_D 1.511 64.0. Morey.
17. Medium flint, n_D 1.613 36.9. Morey.
18. Dense flint, n_D 1.755 27.5. Morey.
19. Dense barium crown, n_D 1.610 57.4. Morey.

The first electric light bulbs were made from a glass containing lead oxide, of which No. 10 is an example. This differs little from a light flint optical glass. It has been supplanted by a glass of the soda-lime type containing significant amounts of both magnesia and alumina, as shown in No. 11.

Laboratory Ware—Laboratory ware requires a high degree of chemical durability and the usual soda-lime types are not satisfactory. One way in which improvement was sought was by increase in silica content and replacement of some soda by potash, as shown in the Kavalier glass (No. 12). The chemical durability was increased in the Jena Geräte glass by replacing some SiO_2 by B_2O_3, and some Na_2O and CaO by ZnO and Al_2O_3 (No. 13). These types of ware have been largely replaced by the Pyrex chemical resistant glass (No. 14) which is fundamentally different from the usual soda-lime-silica composition. It is better considered to be a glass in which the melting point of the silica has been lowered by the addition of B_2O_3 and, in smaller amount, of Al_2O_3, with only the smallest possible amount of alkali. It is intrinsically superior to the best glasses of the soda-lime group in its chemical durability and in its resistance to breakage from heat shock or mechanical strain.

Optical Glass—The optical glasses have the greatest diversity of composition because of the lens designer's need for the widest range of optical properties. They are characterized by almost perfect uniformity of composition and freedom from physical defects, and their quality represents the highest achievement of the glassmaker's art. No. 15 is an ordinary crown, similar in composition to window or plate glass; No. 16 is a borosilicate crown; No. 17 a medium flint; No. 18 an extra dense flint; and No. 19 a dense barium crown, of a type widely used for anastigmat lenses.

The terms "crown" and "flint" are frequently used. Their present usage is inconsistent and they are now chiefly of historical significance. The name "flint glass" comes from the use of flint as a source of silica in a clear glass of good quality, which also contained lead oxide. It now means either a clear, colorless, bottle glass of the type used for dispensing drugs, or a type of optical glass. As applied to optical glass it originally was a glass containing lead oxide, characterized by high index and relatively large dispersion. The term "crown glass" is of uncertain origin. It probably arose either because glass manufacture was a monopoly of the English crown or because the old method of manufacture of window glass was by the "crown" process. It thus denoted a glass of the composition of window glass, and as originally applied to optical glasses was a glass of low refractive index and small dispersion. At present, however, the dividing line between optical crowns and flints is wholly arbitrary, and as applied to some of the newer glasses it is devoid of significance. Similarly, the incongruous term "crystal glass" refers to a clear, colorless glass, often of slightly higher index than ordinary glass because of a small lead oxide content. Glass No. 10, if used for cut glass, might be termed a "crystal" but its lead content is about twice that more commonly used for crystal. The same glass is often used for tubing but many types of glass are worked in tube form.

PROPERTIES OF GLASS

Chemical Durability—The resistance which glass offers to the corroding action of water, atmospheric agencies (primarily water and carbon dioxide), and aqueous solutions of acids, bases and salts is a property of great practical significance, and is denoted by the term "chemical durability." In a large proportion of the uses to which glass is put its power of resisting such attack is the chief reason for its preference over competing materials. An example is the use of glass containers, of which enormous numbers are used for the distribution of commodities ranging from milk to medicine and acids. In this field the superiority of glass leaves it without a competitor. Even in chemical manufacturing, where the requirements are more exacting, glass is being used to an increasing extent as an engineering material because of the resistance which it offers to surface attack under extreme conditions. In other uses of glass chemical durability is a secondary factor, but the requirement of a chemical durability sufficient for the service contemplated, places a limit on the compositions which may be employed. Examples of such uses are those in which glass is chosen for its optical properties. These uses range from windows to lens systems. Although glass used for such purposes is not subjected to as drastic treatment as in the preceding cases, it is essential that there be no appreciable amount of surface alteration.

The necessity of producing glass stable enough to serve the purpose for which it is intended places a practical limit on the compositions which may be employed. The limit set by this requirement differs widely with the use for which the glass is intended. Many glasses possessing desirable optical or mechanical properties are unsuitable because of their susceptibility to corrosion; others may be suitable for optical purposes in protected lens systems and still be worthless for laboratory use. The methods of testing glass thus become of fundamental importance.

Testing—The evaluation of the chemical durability of glass is difficult because the process is not simply one of solution but it is one of decomposition as well. There is no true "solubility" of glass in water. All that can be measured is a rate of decomposition, and rates of reaction differ from equilibrium values because they are highly susceptible to slight differences in experimental conditions. The only true measure of the suitability of a glass in a particular service is its actual use in such service, but it is desirable to have laboratory methods which make it possible to anticipate the results of the service test. Many methods have been proposed, but no one of them is free from serious criticism. All have been developed from the basic thesis that the verdict of actual service may be anticipated by accelerating the corrosive action by the use of more drastic reagents, or by increasing the surface through the use of powders, or by the use of higher temperatures, and by using sensitive methods to detect and measure the resulting action.

The choice of method is determined largely by the use to which the glass is to be put. Methods suitable for differentiating glasses to be used in optical instruments may be far too mild to discriminate adequately between types of chemical glassware. For resistance to attack by acids, the glasses high in SiO_2 and B_2O_3 are best, but they are not necessarily the most resistant to attack by alkaline solutions. Change of temperature at which glasses are tested will frequently alter their order of durability, and may have no relation to their relative excellence in service at ordinary temperature. Our knowledge of the durability of glass, of the factors affecting the durability in the different uses of glass, and of the factors determining the results obtained by the various methods of measuring durability is far too meager to justify positive statements of any but the most general type. The setting up of specifications based on any method of testing should be done only after securing evidence as to correlation of such results with actual service.

PHYSICAL PROPERTIES

The physical properties of glass are determined primarily by chemical composition, but when measured at ordinary temperatures they are affected by the thermal history of the glass. As the glass is cooled from a high temperature some

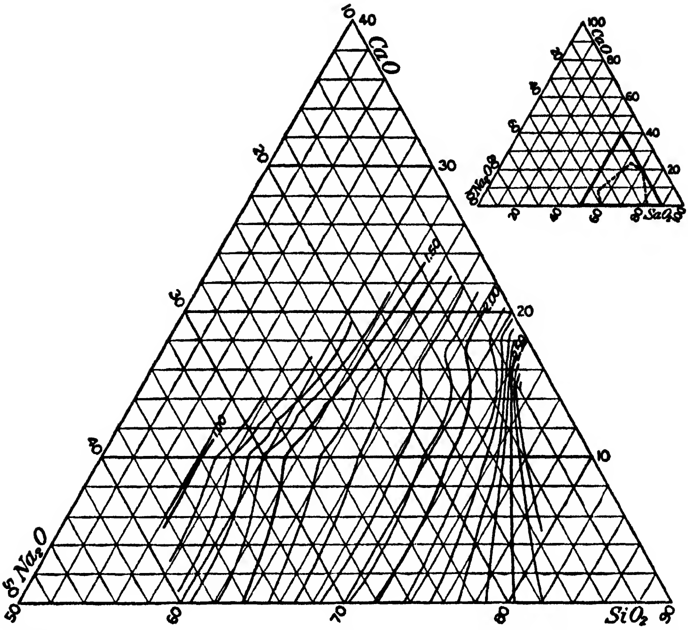

FIG. 5. Isokoms (Lines of Constant Viscosity) in the System Na_2O-CaO-SiO_2 at 1400° C. (After Washburn, Shelton and Libman)

TABLE 2—FACTORS FOR CALCULATION OF PHYSICAL PROPERTIES

Oxide	*Density* [1]	*Coefficient* [2] *of Expansion*	*Heat Capacity* [3]	*Thermal Conductivity* [4]
SiO_2	2.20	0.50	0.1913	3.00
B_2O_3	....	−6.53	0.2272	3.70
Na_2O	3.47	41.6	0.2684	10.70
K_2O	....	39.0	0.1860	13.40
MgO	3.38	4.5	0.2439	4.45
CaO	5.00	16.3	0.1903	8.80
ZnO	....	7.0	0.1248	8.65
BaO	....	14.0	0.0673	11.85
PbO	....	10.6	0.0512	11.70
Al_2O_3	2.75	1.4	0.2074	6.25

[1] Values of d', etc., in: $\frac{100}{D} = \frac{x'}{d'} + \frac{x''}{d''} + \cdots + \frac{x^n}{d^n}$, in which D is the density, x', x'', x^n the percentages by weight of the components, and d', d'', d^n the corresponding density factors. English, S., and Turner, W. E. S. T., J. Soc. Glass Tech. *6*, 228 (1922).

[2] Values of a, etc., in: $\lambda = a_1x_1 + a_2x_2 + \cdots + a_nx_n$; $\lambda = \frac{10^8}{l}\frac{\Delta l}{\Delta t}$. The coefficient for B_2O_3 is limited to the range 0–12 per cent B_2O_3. English, S., and Turner, W. E. S. T., J. Soc. Glass Tech. *12*, 760 (1929).

[3] Values of a_1, etc., in: $c_p = a_1x_1 + a_2x_2 + \cdots + a_nx_n$. Winkelmann, A., Ann. physik. Chem. *49*, 401 (1893).

[4] Values of λ_1, etc., in: $\frac{100}{\lambda} = \frac{b_1}{\lambda_1} + \frac{b_2}{\lambda_2} + \cdots + \frac{b_n}{\lambda_n}$, in which λ = reciprocal thermal conductivity in cal. per sq. cm. per sec. per ° C. per cm.; b_1, etc., are percentages by volume of the several constituents. After Eucken, A., Ann. physik. *34*, 185 (1911).

molecular rearrangement takes place with a general decrease in interatomic distances and possibly an increase in regularity of atomic distribution. At high temperatures and low viscosities this rearrangement is practically instantaneous. As the glass is cooled through the upper part of the annealing range it takes from a few minutes to hours for the glass to become stabilized, and below the annealing range impracticably long times are required for the glass to attain the equilibrium condition. The stabilization affects all the properties of glass, although it is usually a second-order effect. In a precise consideration of the relationship between composition and property it is necessary to define the thermal history. It is not sufficient to state that the glass was well annealed.

Measurement and specification of properties are necessary in design of equipment using glass and for control of process and product. Some properties can be calculated from composition by assuming an additive contribution from each component proportional to the amount of it present, but all such calculations are rough approximations. Most measurements are made at ordinary temperatures, but viscosity and surface tension can be measured only at high temperatures where the glass is in a fluid or molten condition.

Viscosity—Several workers have studied the viscosity of soda-lime-silica glasses, as dependent on composition and on temperature. The measurements of Washburn, Shelton and Libman[6] covered the largest range in composition, but do not agree in magnitude with later workers. Figure 5 represents their results at 1400° C.; Figure 6 shows the effect at 1000° C. of the replacement of Na_2O, CaO, or Al_2O_3, as determined by English, and Figure 7 gives the change in viscosity with temperature of a typical soda-lime-silica glass, as determined by Lillie.

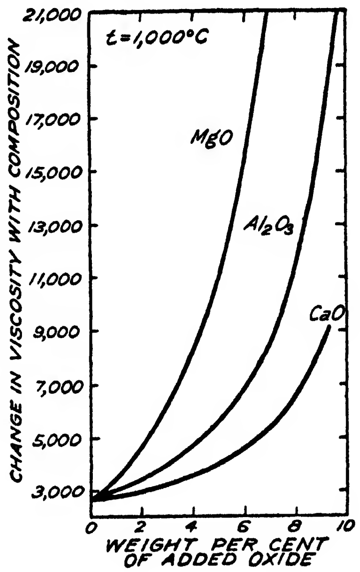

FIG. 6. Effect on the Viscosity, in Poises, at 1000° C. of the Molecular Replacement of Na_2O by CaO, MgO, or Al_2O_3 in the Glass $2Na_2O$, $6SiO_2$. (After English)

The viscosity is of importance in control of glass manufacture. Glass is usually melted at such a temperature that its viscosity is from 10 to 15 poises, and the most favorable temperature for hand-gathering is about 300 poises. The "softening point," an empirically-specified point on the viscosity-temperature curve, is the temperature at which a thread of glass 9 inches long and 0.6 millimeter in diameter lengthens under its own weight at the rate of one millimeter per minute when heated in an electric furnace throughout its upper 9.3 centimeters of length. This corresponds to about 4.5×10^7 poises. The annealing temperature determined by Lillie as 4.7×10^{13} poises is such that internal strain

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[6] Washburn, E. W., Shelton, G. B., and Libman, Univ. of Ill. Eng. Expt. Sta. Bull. 140 (1924).

will disappear by viscous flow in about 15 minutes, and the strain point (viscosity about 10^{14} poises) is such a temperature that there is practically no viscous yield in a short time. At the strain point the glass anneals in about 16 hours, and below it no permanent strain will be introduced if the glass is cooled as quickly as is possible without breaking.

Surface tension is the other property usually considered at high temperatures where the glass is molten. The measurements in the literature are not concordant. They usually agree in that the surface tension is not greatly changed by change in composition, and that the temperature coefficient is small and negative, of the order of 0.01 to 0.04 per cent per degree. The best value of the surface tension of ordinary soda-lime-silica glasses is about 300 dynes per centimeter at 1200° C. Glasses high in B_2O_3 or in PbO have lower surface tensions.

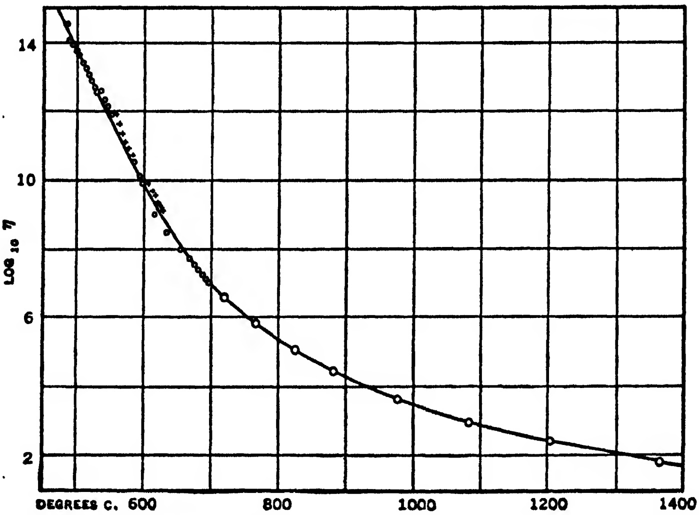

FIG. 7. Change in Log Viscosity, in Poises, over a Large Range of Temperature. (After Lillie)

Calculation of Physical Properties—Certain of the physical properties in multicomponent glass systems are sufficiently close to being additive that they may be computed by appropriate simple relations. A summary of the constants and the relations is given in Table 2.

Density is the property of glass most frequently measured and numerous measurements have been made of glasses of widely differing compositions. Within the narrow composition range of most soda-lime-silica glasses, calculation of density by means of additive factors should give a fair approximation to the correct value. These factors are those in the formula

$$\frac{100}{D} = \frac{x'}{d'} + \frac{x''}{d''} + \cdots \frac{x^n}{d^n}$$

in which D is the density, x', x'', . . . x^n the percentage by weight of the components, and d', d'', . . . d^n the corresponding density factors. Table 2 gives the factors given by English and Turner. When precise results are required measurements of the desired glass are usually necessary, and in that measurement account must be taken of the effect of thermal history. Many standard types of glass, such as Pyrex resistant laboratory ware and Jena 59^{III}, are of such widespread use that their density becomes a matter of general interest. Fortunately such glasses usually are constant enough in composition for the density given in Table 3 to be used for all but the most exacting work.

TABLE 3—PROPERTIES OF SOME MULTICOMPONENT GLASSES

Density *g./cm.*^{3}	*Young's Modulus*	*Poisson's Ratio*	*Tensile Strength*	*Compressive Strength*	*Thermal Expansion* $\frac{10^6}{l}\frac{\Delta l}{\Delta t}$	*Specific Heat* *g.-cal./g.*
	Unit = 1 kilobar; 1 bar = 14.50 lb./in.^{2} *= 1.020 kg./cm.*^{2}					
2.25	611	......	....	....	3.2 (19–350°)	0.20
2.370[1]	715[2]	0.197[4]	0.68[1]	12.4[1]	....	0.204[2]
2.370[1]	711[2]	......	....	....	5.90 (0–100[6]	
2.5[3]	644[2]	0.221[4]				
2.47[3]	731[2]	0.210[4]				
......	....	......	....	....	8.83 (18.7–90.5)[6]	
2.580[1]	647[2]	0.231[4]	0.66[1]	9.0[1]	9.63 (17–95.5)[5]	
3.21[3]	727[2]	0.252[4]	....	....	7.90 (18.9–93.1)[5]	
3.532[1]	783[2]	0.271[4]	0.73[1]	8.3[1]	....	0.140[2]
4.731[1]	537[2]	0.239[4]	0.52[1]	6.6[1]		
2.585[1]	732[2]	0.228[4]	....	....	8.03 (14.6–92.2)[6]	0.209[2]

[1] Winkelmann, A., and Schott, O., Ann. physik, Chem., *51*, 697 (1894).

[2] Winkelmann, A., Ann. physik, Chem., *49*, 401 (1893).

[3] Zschimmer, E., in Doelter, C., "Handbuch der Mineralchemie," *1*, 869; Dresden and Leipsig, 1912

[4] Straubel, R., Ann. Physik Chem., *68*, 369 (1899).

[5] Pulfrich, C., Ann. Physik Chem., *45*, 609 (1892).

[6] Hovestadt, H., "Jena Glass," Macmillan, New York, 1902.

1. Pyrex chemical resistant glass. Compn. No. 14, Table 1.
2. Borosilicate crown optical glass, $n_D 1.496$, $\mu 64.4$.
3. Thermometer glass 59^{III}.
4. Borosilicate crown optical glass. Compn. No. 16, Table 1.
5. Silicate crown optical glass, $n_D 1.517$, $\mu 60.2$.
6. Light barium crown optical glass, $n_D 1.573$, $\mu 57.6$.
7. Dense barium crown optical glass, $n_D 1.610$, $\mu 57.4$.
8. Dense flint optical glass. Compn. near that of No. 18 Table 1.
9. Thermometer glass, 16^{III}.

Coefficient of Expansion—The rate of expansion of glass with temperature is of scientific and technological importance, and the coefficient of expansion is a property of glass which is greatly affected by change in composition. The rate of linear expansion of glass with temperature is almost constant over a temperature interval up to the annealing range of the glass. More accurate measurements, however, require equations of three or more constants to represent them, and when such high accuracy is in question the thermal history of the glass becomes of importance. In the temperature region in which the expansion is approximately a linear function of temperature the coefficient of expansion, $\lambda = \frac{10^8}{l}\frac{\Delta l}{\Delta t}$, in which l is length, t is temperature, may be calculated roughly on the assumption of additivity by means of the equation

$$\lambda = a_1x_1 + a_2x_2 + \cdots a_nx_n$$

in which $x_1, x_2, \ldots x_n$ are the percentages by weight of the several constituents and $a_1, a_2, \ldots a_n$ their specific factors, given in Table 2. Expansion coefficients of some typical glasses are in Table 3.

Elasticity—When a piece of glass is strained by an applied force it returns to its original size and shape on removal of the force, provided that the temperature is not too high and that the force is neither too great nor applied for too long a time. The property by which the glass regains its original dimensions is called elasticity and is measured by the ratio of the stress to the strain. The constant of proportionality for each type of stress is a property of the substance. The stress may be applied in various ways: for example by hydrostatic pressure, producing a pure compression in which the elasticity is measured by the bulk modulus K; by torsion, producing a shear, in which case the elasticity is measured by the modulus of rigidity R; or by bending or tension, both of which produce both compression and shear. The modulus of extension in tension is known as Young's modulus, E; the ratio of lateral to longitudinal strain under unidirectional strain is Poisson's ratio, σ. These four quantities are related by the formulae

$$E = 9KR/(3K + R) = 3K(1 - 2\sigma) = 2R(1 + \sigma)$$

Most of the data in the literature refer to multicomponent glasses, representative examples of which are given in Table 3. Factors have been given for the calculation of Young's modulus from composition, but both the experimental and theoretical foundations for such factors are inadequate and the results of such calculation are too unreliable to justify their inclusion here.

Strength—When glass is subjected, for short periods, to stresses within the limits of elasticity, the resulting strain disappears after the removal of the stress, and the piece returns to its original dimensions. With most substances, on addition of load beyond the elastic limit, a condition is reached in which yielding takes place continuously, and if the load is maintained, fracture results. A substance in which there is an initial elastic limit, that is, which is not viscous, is said to be in a condition of plasticity in the region beyond the elastic limit in which deformation takes place continuously. With glass, there appears to be no region of plasticity and Hooke's law holds up to the breaking point of the glass. There is no accepted relation between the elasticity of a substance and its ultimate strength. A high value of Young's modulus does not necessarily imply a large tensile strength, nor does a high modulus of compressibility imply a large crushing strength. Also, glass may be broken in any one of many different ways, by tension, compression, twisting, or impact; but there is no connection between the numerical values of the breaking strengths as determined by these several methods. Indeed, it is probable that in all the various methods of applying stress to glass, fracture always takes place in tension. A failure in uniform compression is unthinkable, and fracture results from tensile stresses developed by the manner of applying the load.

The strength of a great number of glass samples has been measured, but much uncertainty exists as to the significance of the results. Observed strengths are greatly influenced by the size and shape of the sample. With fine fibers, strengths up to three million pounds per square inch have been observed.

From theoretical considerations there is reason to believe that the strength of glass in tension should be that required to overcome the molecular cohesion, about three million pounds per square inch, but the values found in practice are always far smaller than this hypothetical limit. The reason is usually to be found in the effect of surface flaws or cracks which concentrate the stress at the point of the flaw and thus determine the point of breakage. The strength of glass is determined by the weakness of its surface, and in tempered glass such as is sometimes used in windshields the strength is increased by a heat treatment by which the surface is put under strong compression.

Factors have been proposed for calculating the strength of glass from its composition, but they are of little value. Experience has shown that a tensile strength of about 0.7 kilobar (10,000 lb. per sq. in.) is a fair estimate of the strength to be expected, although larger values are frequently found. In general engineering calculations a factor of safety of 4 or 5 should be allowed when this value of the tensile strength is used.

Little is known about the effect of temperature upon the strength of glass. At ordinary temperatures the strain remains proportional to the stress until the specimen breaks. At high temperatures the diminution of viscosity makes the strength evanescent for loads of a duration decreasing with increasing temperature. This is illustrated by the results obtained by Laubengayer, given in Table 4, on the collapsing temperatures of glass tubes of 13-mm. bore and 1.8-mm. wall thickness, heated at 3° C. per minute, either open to the air or evacuated to 3-mm. pressure.

TABLE 4—COLLAPSING TEMPERATURES OF GLASS TUBES *

	Temp. (° C.)	
Glass	*Open*	*Evacuated*
Soft soda-lime	700	585
Resistance tubing	750	635
Pyrex chemical resistant	820	670
Bohemian combustion	860	740
Moncrieff combustion	820	770

* Laubengayer, A. W., Ind. Eng. Chem. *21,* 174 (1929).

Thermal Endurance—The ability to withstand thermal shock resulting from sudden change in temperature is important in many uses of glass, and methods of measuring thermal endurance find application in the routine testing of glassware. Several formulas have been developed for the calculation of thermal endurance from those properties of glass which affect (1) the development and distribution of strain and (2) failure under stress. These properties include thermal expansion, Young's modulus, Poisson's ratio, thermal conductivity and diffusivity, and tensile strength. It is doubtful if the use of any of these formulas in comparing glasses offers any advantage over the comparison of expansion coefficients alone. The coefficient of expansion is more affected by change in composition than are Young's modulus, Poisson's ratio, or the tensile strength. Moreover, since the strength of glass is largely determined by surface conditions, the breakage of glasses of similar expansion properties under thermal shock will be determined largely by the condition of their surfaces.

Heat Capacity—The specific heat of glass is assumed to be an additive function of the constituent oxides, and this is more nearly true for specific heat than for any other property. The factors given in Table 2 for calculation of specific heat are those of Winkelmann[7] and represent values of the coefficients a', a'', . . . a^n in the formula

$$c_t = a'x' + a''x'' + \cdots + a^nx''$$

in which x', x'', x^n are the percentages by weight of the constituent oxides.

The specific heat of Pyrex resistant laboratory glass[8] in the interval from 0-265° C. may be calculated from the formula

$$c_t = 0.174 + 0.00036t$$

in which c_t indicates the specific heat at $t°$ C.

Thermal Conductivity—There has been little systematic study of thermal conductivity of glass. It is usually considered to be additive, and Table 2 gives coefficients proposed by Russ.[9] These coefficients are the values of $\lambda_1, \lambda_2, \ldots \lambda_n$ in the formula

$$\frac{100}{\lambda} = \frac{b_1}{\lambda_1} + \frac{b_2}{\lambda_2} \cdots \frac{b_n}{\lambda_n}$$

in which λ is the reciprocal of thermal conductivity and $b_1, b_2, \ldots b_n$ the percentages by volume of the constituent oxides. The unit is the gram calorie per square centimeter per second per degree C. per centimeter. Stephens[10] measured the change in thermal conductivity with temperature of Pyrex resistant laboratory glass from −181° to 250° C. His results are represented by

$$K = -0.003523 + 0.002454 \log_{10} T$$

in which K is thermal conductivity, T, the absolute temperature. At 20° the experimental value of thermal conductivity was 0.00245; at 90°, 0.0027.

MANUFACTURE OF GLASS

THE RAW MATERIALS

The raw materials of glass manufacture are chiefly sand (SiO_2), soda-ash (Na_2CO_3), and lime ($CaCO_3$), with smaller amounts of many other substances.

Sand—Quartz sand is the chief raw material in glass manufacture. It is usually shipped in paper-lined box cars after purification at the plant. The treatment necessary depends on the source of the sand, that is, whether from hard or decomposed quartzite, sandstone, or unconsolidated beds. The harder rocks are mined by blasting, crushed first in jaw crushers, then in gyrating crushers, and finally in a water-fed chaser mill. The crushed material after passing through revolving screens to remove coarser particles, usually those larger than 20-mesh, is washed to remove organic material, clay, and fines smaller than 100-mesh, then drained, dried, and passed through magnetic separators.

The chief impurities in glass sand are: iron oxide, titania, alumina, calcium

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[7] Winkelmann, A., Ann. physik. Chem. *49*, 401 (1893).

[8] Hildebrand, J. H., Dushak, A. D., Foster, A. H. and Beebe, C. W., J Am. Chem Soc. *39*, 2293 (1917).

[9] Russ, A., Sprechsaal *61*, 887 (1928).

[10] Stephens, R. W. B., Phil. Mag. (7) *14*, 897 (1932).

carbonate, and zirconia. Of these, iron oxide is the only one usually objectionable. For the best grade optical glass the total iron (expressed as Fe_2O_3) should be less than 0.01 per cent, and for the best grade of tableware, less than 0.035 per cent. As the necessity for freedom from color decreases, the permissible iron content increases, and for some types of bottles 1 per cent is not objectionable.

Sources—Glass sand is obtained in 23 states, and the total production in 1939 was 2,207,085 tons. Two-thirds of the total production was, in order of importance, in West Virginia, Illinois, and Pennsylvania; 20 per cent was in New Jersey, Missouri, and Indiana.

The production in West Virginia and Pennsylvania was chiefly from the Oriskany formation, a thin but widespread layer of sand outcropping across New York and along the Appalachian region from New Jersey to Alabama. It represents the shallow shores of an inland sea which in lower Devonian time extended from the St. Lawrence valley along the course of the present Appalachian Mountains as far south as Alabama. It consists of remarkably pure quartz grains cemented by a calcareous cement, and in places in which the cement has been dissolved away the rock crumbles into friable sand.

The glass sand produced in Illinois, Missouri, and Indiana comes chiefly from the St. Peter sandstone. This formation was laid down from Minnesota to Oklahoma in shallow seas of lower Ordovician age, and is considered to be derived from Cambrian sandstones of windblown origin deposited in the Croixian Sea. It is the great water-bearing formation over a large area, and the circulating waters have in many places completely removed the calcareous cement, leaving a rock which crumbles at the touch. In the Ottawa, Illinois, district it is mined by hydraulic methods; in Missouri in both open-pit and underground mines. Purification includes working, screening, and separation of iron.

The location of glass plants in southern New Jersey was determined by the easily accessible beds of unconsolidated sands, which usually are mined by suction dredges, followed by the usual purification processes.

Soda Ash—The chief source of sodium oxide in the glass industry is soda ash made by the Solvay process.[11] The consumption by the glass industry in 1939 was 744,275 tons. The chief impurity is sodium chloride, which should be less than half of one per cent. The second source of sodium oxide is sodium sulfate or salt cake, of which 38,287 tons were used in 1939, usually together with the carbonate. If the sulfate is used in large quantity, carbon in some form is added to reduce it. In smaller quantities it is added to help fining and to reduce scum. Potash usually is added as $K_2CO_3 \cdot 1\frac{1}{2}H_2O$. In 1917 the lack of a domestic source of K_2CO_3 was a serious handicap in the production of optical glass for fire-control instruments, but there is now an ample supply.[12]

Calcium Oxide—Calcium oxide is added as limestone (the carbonate), as burnt lime (CaO), or as unslaked lime ($Ca(OH)_2$). The choice appears to be based on personal preference. Most limes used in the United States are dolomitic, and the presence of magnesia in the dolomite ratio is common in America, especially in bottle glass. In 1939, the consumption of lime in the glass industry was

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[11] See Chapter 10.

[12] See Chapter 9.

214,255 tons; of limestone, 216,492 tons. For finer grades, especially optical glass, precipitated calcium carbonate is used.

MISCELLANEOUS INGREDIENTS

Alumina—Alumina is sometimes added as precipitated alumina, made by precipitation from a solution of the sodium aluminate. This is the form of alumina used when a minimum iron content is necessary. In general practice alumina is added as a mineral, usually nephelite, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, or feldspar, a mixture of orthoclase, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, and albite, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$. In 1939 the glass industry used 165,911 tons of feldspar. The original state of combination of the alumina does not affect its influence on the properties of glass, and the choice of mineral is determined by the ultimate cost, purity, and amount and desirability of other mineral constituents. Alumina in amounts from one-half to two or three per cent is a desirable constituent of glass, especially in its influence in decreasing the tendency toward devitrification, and increasing chemical durability.

Boric Oxide—Boric oxide is frequently added to the usual glass types in the amount of one per cent or less, to increase the rate of melting and to improve chemical durability. It is used in larger amounts in the borosilicate crown optical glasses, and especially in low-expansion glasses such as Pyrex chemical resistant glass. When the soda content is not objectionable it is added as borax, $Na_2B_4O_7 \cdot 10H_2O$, or as anhydrous borax, supplied in crystalline form. When the Na_2O content is not wanted, boric acid, H_3BO_3, is used. In either case a high purity product is obtainable.[13]

Nitrate—Sodium nitrate or, in some batches, potassium nitrate, is frequently added for its oxidizing action. Either product can be obtained in satisfactory purity. Sodium chloride is sometimes present as an impurity in soda ash, and is sometimes added as a fining agent.

Oxides—Lead oxide is usually added as litharge, PbO, as red lead, Pb_3O_4, or as a lead silicate. Red lead is used to secure oxidizing conditions in the melt, but the same condition is easily insured by other means. The chief impurity in lead oxide is alkali oxide, usually in amount insignificant for ordinary glassmaking. Zinc oxide is used as the sublimed product, easily obtained of adequate purity. Barium oxide when used in large proportion is added as barium carbonate; when used in small proportion barium sulfate is used for the effect of the sulfate as a fining agent. The carbonate is made from the sulfate by reducing to sulfide, dissolving, and precipitating with sodium carbonate. The remaining sulfide is the chief impurity. Arsenic oxide is added to many glasses as a fining agent, and when purified by sublimation it is satisfactory as purchased.

Cullet—A large proportion of the charge of a furnace consists of broken glass, called cullet. The proportion used varies widely, from 10 to 75 per cent, depending on the amount of scrap glass available and the practice of the operator. It is generally believed that a generous proportion of cullet speeds up melting and produces a more uniform product. When there is not enough scrap being returned, scrap glass is purchased or a furnace may even be run to produce

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[13] See Chapter 9.

dient is introduced at the softening point, at which the glass yields quickly under stress, no strain will result from introduction of the temperature gradient, the glass will cool free from strain until the temperature gradient is removed, and the removal of the temperature gradient will produce a permanent stress. The permanent stresses in poorly annealed glasses are developed by the removal of a temperature gradient at low temperatures, and the amount of this stress is the difference between that caused by the removal of the temperature gradient, which produces a compression on the surface, and the temporary strain carried down from the high temperature at which the gradient was introduced. In short, the permanent stress is equal and opposite in sign to the stress lost by flow in the first part of the cooling.

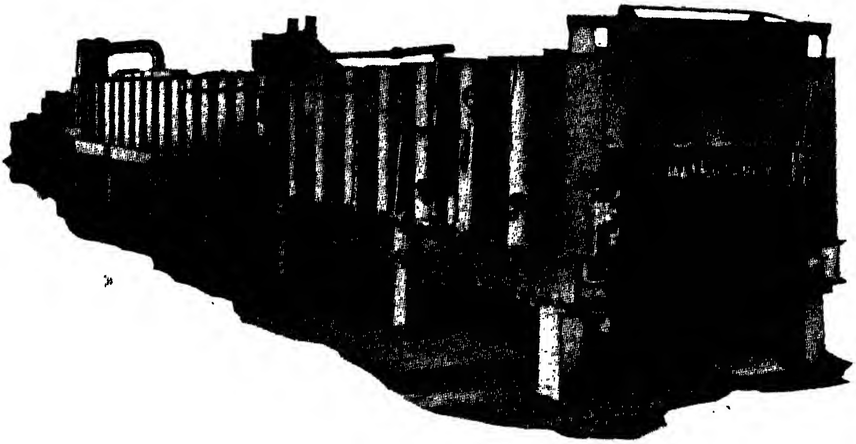

Fig. 11. Commercial Annealing Lehr for Glassware. (Courtesy Hartford-Empire Co.)

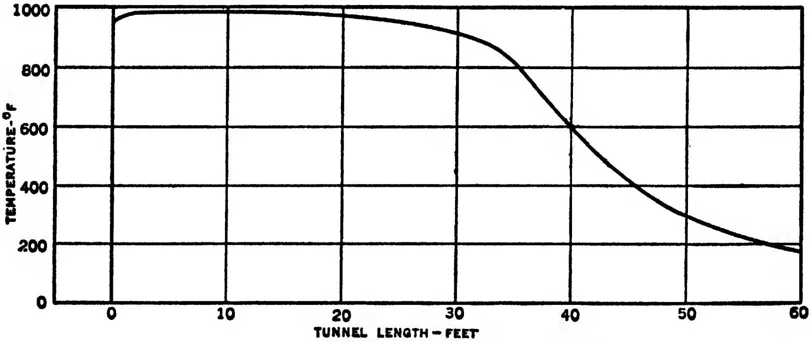

Fig. 12. The Distribution of Temperature in an Annealing Lehr. (Courtesy Hartford-Empire Co.)

The annealing of glass has been exhaustively treated both experimentally and mathematically by Adams and Williamson,[16] who have given explicit directions

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[16] Adams, L. H. and Williamson, E. D., J. Franklin Inst. *190,* 597 and 835 (1920).

for the most efficient cooling process in terms of the properties and dimensions of the glass. The critical part of the cooling is in the first establishment of the temperature gradient, and in general the thicker the piece the lower the temperature at which it is advisable to remove stress. Naturally, the time must also be increased, but the loss in time is made up by the greater initial cooling rate.

A typical commercial annealing lehr is shown in Figure 11. Figure 12 shows the change in temperature with distance in a lehr used for annealing bottles. The front part of the lehr is usually heated by gas. Where the "bloom" on the ware caused by sulfur in city gas is objectionable, either natural or propane gas is used, and electrically-heated lehrs are in development. The delivery end of the lehr is not heated and is usually lower than the front end in order to aid in controlling convection, which usually should be from the cold to the hot end. The ware is carried through the lehr on a woven wire belt.

GLASS PRODUCTS

Hand Manufacture—The manufacture of glass throughout the centuries has evolved from a small-scale handicraft to a scientifically-controlled, mechanized, mass-production industry. Many phases of the industry, however, are still dependent on the skill of the glass-blower. Even in the highly-mechanized container industry, special shapes which are used in too small quantity to justify the expense of putting on a machine, are blown by hand. The value of hand-blown ware is about 50 million dollars, or one-seventh of the total of all glass production.

Free Blowing—The process by which glass is shaped entirely by hand-blowing and manipulation of the hot glass without the aid of molds is known as free-blowing or off-hand blowing. It requires a high degree of skill, and the finest products of the glass-blower's art are free-blown. The molten glass is gathered on a glassmaker's pipe, roughly shaped or "marvered" by rolling on a slab of iron, then given final shape by blowing and hand-shaping with simple tools. Parts not produced by simple blowing, such as stems, handles, and feet, are welded into the main piece.

Blowing in Molds—Much glass is hand-blown in a mold. Paste-molds of metal, lined with a paste of resinous material, coated with flour or other organic powder which will char and leave a carbonaceous lining, are used for thin ware of circular cross-section. For simple forms the mold is often of one piece, but usually it is of two parts opening on a hinge. The hot gather is formed by marvering, placed in the mold, and the pipe rotated while the piece is blown. The mold is used wet, and the layer of steam formed by the hot glass acts as a cushion which prevents the glass from coming into actual contact with the mold. The product has a good polish and is usually free from mold marks. Unlined molds of cast iron, usually in two parts, are employed for much large-scale production of shapes that do not require high polish or freedom from mold marks. To prevent wrinkles or ripple marks the molds are kept as hot as is possible without formation of too much scale. Ware blown in a mold, either paste or cast iron molds, often requires a subsequent finishing operation. Some ware is gathered by hand on an iron rod, called a pontil, then pressed without blowing.

In the making of hand-drawn tubing a bubble is blown in a gather of suitable size, and the gather is then marvered into cylindrical shape. It is then manipulated by rolling and blowing so that the bubble becomes a cylindrical hole extending almost to the free end of the gather. This free end is then stuck on an iron rod and pulled into a tube by the carrier who walks away carrying the hot mass of glass, while the blower controls the roundness of the tube by blowing and manipulating the gather. Thickness of tube is controlled by the rate of drawing, and local hot-spots at which the tube tends to draw down are controlled by fanning.

Machine-made Ware—The mechanical processes used in working glass differ widely according to product. The first branch of the industry to be considered is flat glass, consisting chiefly of window and plate glass, and laminated glass used for automobile glazing.

Window Glass—Window glass, formerly made by the cylinder process, is now almost entirely made by drawing in flat sheets directly from the tank. In the Fourcault process the sheet is drawn through a "debiteuse," which is a clay block sunk to a varying depth into the molten glass, and containing a longitudinal slot through which the glass rises under a slight head. The slot is four to six feet long, and the sheet is pulled up by rollers which are as wide as the full width of the sheet. The sheet is drawn at exactly the rate at which the glass rises through the slot under the slight head, thus avoiding the narrowing effect of surface tension, and the thickness is determined by the rate of drawing, which, for a single-strength sheet, 80 inches wide, is 48 inches per minute. The sheet is drawn vertically through an annealing zone and then cut into standard lengths.

In another process, used by the Pittsburgh Plate Glass Company, the sheet is drawn vertically without the aid of a debiteuse. In the Colburn process, used by the Libbey-Owens-Ford Company, the glass may be drawn directly from the tank over bending rolls, then horizontally on a flattening table, and through an annealing chamber. The product of these continuous sheet processes is greatly superior to the older glass; so much superior that flat-drawn glass is replacing polished plate in some of its uses.

Plate Glass—By plate glass is meant a sheet that has been ground and polished. Much plate glass, including all large sheets, is still made in individual pots, which are lifted from the furnace, the glass being poured onto an iron casting table. A heavy iron roller flattens the glass into a sheet, which is then annealed, inspected, and cut into sheets. These sheets are then ground and polished.

In the Bicheroux process the glass is poured from the pot onto a set of power rollers, and in some plants the glass flows directly from the tank through rollers. Wire glass is made by a process similar to that for plate glass except that a sheet of woven wire is rolled into the glass. "Cathedral" glass is cast with a rough, usually figured, surface and is not ground.

Safety Glass—Automobile glazing is estimated to consume 75 per cent of the output of plate glass. At first windshields and windows were of ordinary plate, then safety glass came to be used in the windshields, and now all glass is usually of a safety type. Two types of safety glass are used. One, known in this country as "Herculite" or "Tuf-Flex," is a polished plate glass that is thermally toughened by being heated just below the softening point and then chilled by a large number of jets of air on each side to produce a surface compression and a strain pattern of a definite checkerboard type. The enormous increase in strength is spectacular, as shown by the familiar illustration of several men standing on a windshield supported at the two ends, or by a sheet being used as a diving board. Like any material, however, it can be broken, but the particular strain pattern used makes the broken glass practically harmless. Ordinarily, when glass breaks it develops sharp, jagged splinters, but the heat-treated safety glass dices into shapes best described as octahedral with edges repeatedly truncated, and free from sharp edges. About 13.5 million square feet of this type safety glass were produced in 1940.

Other safety glass is made like a sandwich, with a layer of an organic plastic between two layers of glass. The first laminated glass used cellulose nitrate or cellulose acetate,[17] but this was not entirely satisfactory because of the effect of light in turning it brown and spoiling its plasticity, and because it became brittle at low temperatures. Newer plastics,[18] vinyl butyrol and methyl methacrylate, have overcome these difficulties, and now laminated glass is used in the greater part of the automobile industry, in airplanes, and for bullet-resisting glass.

In the manufacture of laminated glass the glass and plastic are cut to shape, inspected, washed, an adhesive applied to the glass if such a step is necessary, and the sandwich assembled. The parts are pressed together at moderate temperature and pressure, and then given a final treatment in an autoclave at about 250 pounds pressure to weld the plastic and glass firmly together. After pressing, the edges are cleaned and given a finishing operation to seal them, except with such plastics as are not affected by moisture. The outermost glasses of the laminated light should be as thin as possible to avoid undue spalling when broken. In some of the production the laminated glass used is flat-drawn sheet glass, which is not as flat as plate glass and consequently does not give such completely satisfactory vision.

Tubing—The first mechanization of the manufacture of glass tubing was in the provision of towers for drawing. The large hand gather is marvered as in the hand drawing, stuck on, and then fastened to a vertical elevator which draws the tube at a uniform rate in a closed chamber. This process is much used for thermometer tubing where uniformity of bore is essential. The white backing is marvered into the gather.

True mechanical drawing of tubing takes the glass directly from the furnace. In the Danner process the glass flows onto a hollow revolving mandrel through which air is blown. The glass wraps itself around the mandrel and flows together. The drawing process is started by hand; the tube being drawn off the mandrel and fastened to a pair of asbestos-covered belts which draw it continuously. In another process the tube is drawn upward through a circular clay block floating on the glass, while air is blown upward through the center of the block.

Hollow Ware—The various types of glassware, including plates, dishes and cups, tumblers and goblets, lamp chimneys, globes and reflectors, ovenware, and the wide variety of containers, are made by one of two types of machine. One type is the suction-feed Owens machine, the pioneer machine in this field which started the wholesale mechanization of the industry; the other type is the gob-feeder machine, of which there are several variants.

[17] See Chapter 38 and Chapter 31.
[18] See Chapter 31.

The Owens machine (Figure 13) is a self-contained, synchronized, circular assemblage of a number of units or arms, which takes glass out of an auxiliary circular revolving pot fed from the main tank. In its operation a suction mold is lowered onto the molten glass, a gob of the requisite size is sucked up, and the excess glass cut off. The suction-mold then swings away, leaving a shaped gob called a parison suspended from the neck-mold. The blow-mold then rises to surround the parison, and the bottle is blown. The suction-mold repeats its cycle. The blow-mold delivers a finished bottle and again rises into position to take another parison from the suction-mold. For large ware, each arm has a single mold, but for smaller bottles a double or triple cavity mold which shapes two or three bottles at once, can be used. With double molds a 10-arm machine can deliver 100 6-ounce bottles per minute, or 1000 gross per day, to the annealing lehr.

Fig. 13. The Owens Machine. (Courtesy Owens-Illinois Glass Co.)

Most other types of automatic machines make use of a feeder, which delivers hot glass in gobs of predetermined shape and weight at regular intervals to a forming mold. Numerous problems arise in accomplishing this apparently simple purpose, and differences in their solution characterize the several types of feeders. Feeders are an integral part of the "blow and blow" and "press and blow" machines on which are made the larger part of all hollow ware. In these latter type machines the gob is formed into a parison by pressing in the feeder mechanism and then blown into a mold. The two units may be separate or integral.

An example is the Hartford-Empire I S Machine (Figure 14). This is an assembly of several units, each of which is an independent section and may deliver different shapes, provided each requires the same weight gob. The parison molds receive gobs distributed in turn from a single feeder. These molds form the parison, then swing across the table and deliver the half-formed blanks to blow-molds. The rate of production depends on the size and type of ware and the number of sections. With an 8-ounce bottle a 10-section machine may deliver 2000 gross per day.

Several types of automatic presses in which no blowing operations are required are used in connection with feeders in the production of tumblers, dishes, ovenware, tableware, and some packers' ware. In some cases the ware requires finishing by fire-polishing, but much goes directly to the annealer.

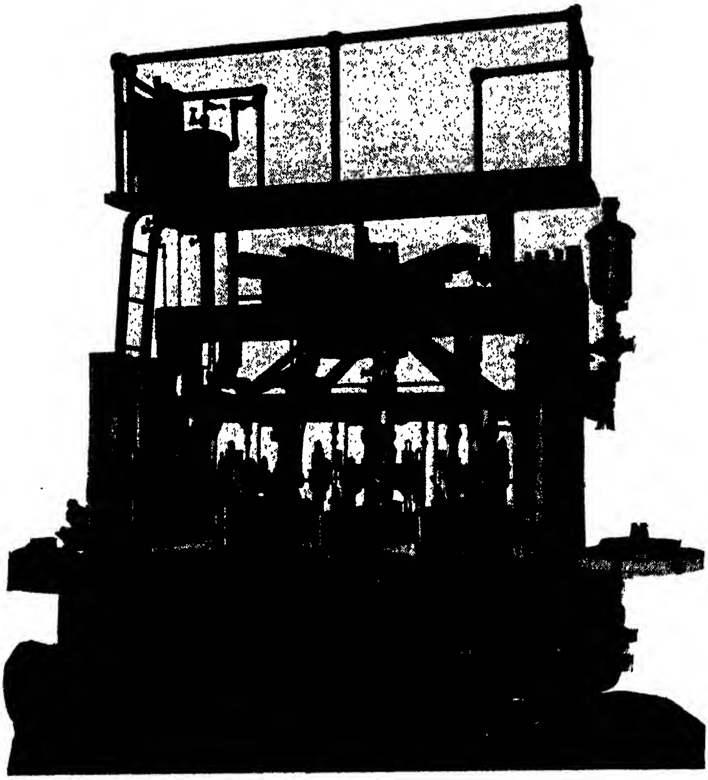

Fig. 14. The Hartford-Empire I S Machine. (Courtesy Hartford-Empire Co.)

Lamp Bulbs—Most lamp bulbs are made on the Corning "399" machine (Figure 15), a ribbon machine which has also been used for bulbs for Christmas tree ornaments and for tumblers. The glass flows in a continuous stream from the forehearth of a tank and passes between two rollers which deliver a continuous narrow ribbon of glass. One roller has depressions on its surface, giving a series of uniformly spaced buttons along the ribbon, which fit over the successive openings in an endless metal belt. The ribbon of molten glass is carried by the belt in a straight line under a row of blow-heads, forming a second endless chain moving in time with, and above, the first. As the belt moves on, the glass buttons sag through the openings in the belt and the blow-heads register above them, after which each lengthening bulb of glass is enclosed from below by a split rotating metal mold which is paste-lined. The bulb is blown as it moves forward in its place in the line by air admitted from the wind-box. After the bulb has cooled enough to maintain its shape, the molds open, as shown in the lower part of Figure 15, and the bulb is separated from the glass ribbon and directed into an annealing chamber. This machine has produced as high as one million bulbs in 24 hours, an excellent illustration of the manner in which mechanism in the industry has greatly reduced the price of an improved product.

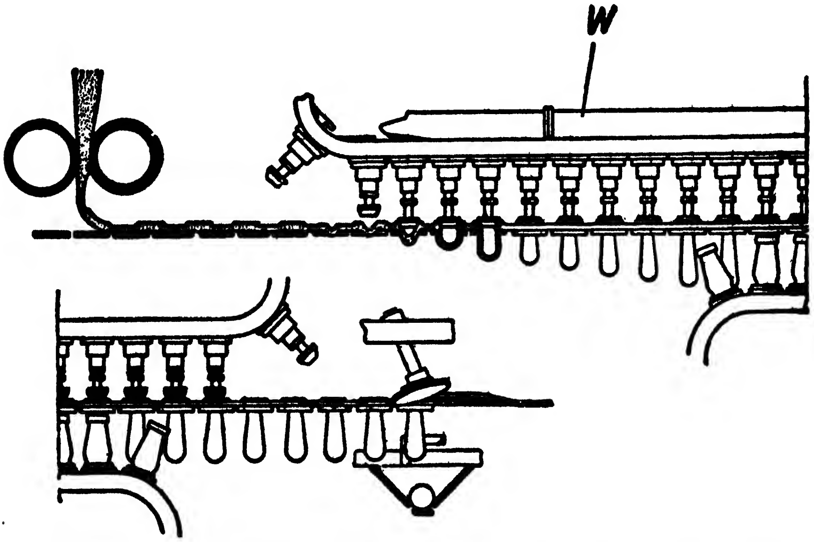

FIG. 15. The Corning "Ribbon" Machine. (Courtesy Corning Glass Works)

Glass Wool—"Fiberglas" is a new product whose manufacture does not resemble any process yet described. Glass fibers have long been known. However, the modern development, by the Owens-Corning Fiberglas Corporation, has been not only one of method of manufacture, but also one of greatly enhancing the usefulness of glass fibers by decreasing their diameter. Much of the older material was little more than thin glass rod. The modern product is smaller in diameter than any other industrial fiber. The industry has been expanding rapidly since its inception a few years ago. The most recent estimates indicate an annual production of over 30,000 tons.

Two processes are used in the production of "Fiberglas," the trade-mark name for the product. Continuous filament is produced by mechanical drawing of the molten glass into strands of indefinite length (measured in miles). The average diameter of the individual fibers is 0.00022 inch, but the filaments from 102 or more orifices are drawn into a strand without twist. After spraying with a lubricant, one or more strands are twisted together to form yarn, and the yarns are plied by twisting two or more together to provide any desired thread or cord construction. The continuous filaments are smooth and cylindrical, and the yarn is free from fuzziness.

Properties of Fiberglas. The fibers owe their properties to their extreme fineness, which is of the order of five ten-thousandths of an inch. The tensile strength of glass fibers increases rapidly as the diameter decreases, and especially as it decreases below two-thousandths of an inch. Strengths as high as one and a half million pounds per square inch have been obtained on fibers of about one ten-thousandth of an inch in diameter. Combined with high strength is extreme flexibility and softness to the touch. It has been calculated that a fiber two ten-thousandths of an inch in diameter has a length of 23 million feet, or 4356 miles per pound, and a total area of 1500 square feet. With so large a ratio of surface to mass, the properties of the surface, and especially its chemical durability, become of utmost importance. The composition of the glass must be such as to have unusual resistance to weathering and to attack by chemical reagents. Glasses have now been developed which will give satisfactory service even under extreme conditions. These are usually soda-lime-silica glasses, low in soda, and containing Al_2O_3 or B_2O_3 or both. Some alkali-free glasses are in use.

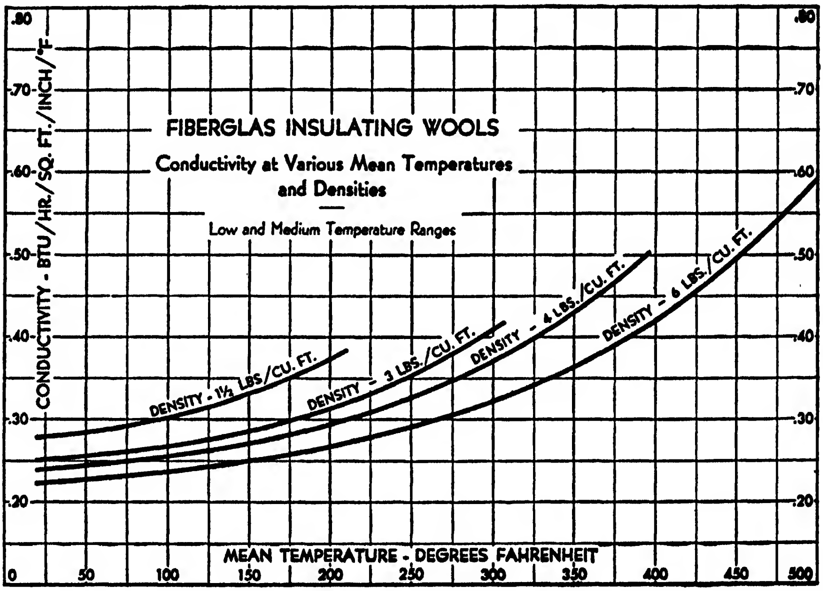

FIG. 16. Thermal Conductivity of Fiberglas Insulating Wools. (Courtesy Owens-Corning Fiberglas Corp.)

Staple Fibers. In the manufacture of staple fibers, molten glass flowing from a multitude of fine holes is met by jets of high-pressure steam which break each stream into a large number of fibers, each so fine as to be almost invisible, and essentially endless. If it is to be used as a yarn, the fibers are sprayed with a sizing or lubricant, as in other textile operations, then gathered into strands which may contain 60 or more individual filaments. In the manufacture of yarn, several of these strands are combined to form a thread, and two or more of the threads are combined with a reverse twist. The resulting yarn is free from any tendency to kink, and its further treatment is the same as that of any other textile material.

This yarn has many uses. It may be spun into cloth, used for dresses, for non-flammable curtains and hangings, as a filtering medium in filter presses, or as a separator in storage batteries. Decorative yarns, in which the coloring material is a part of the glass itself, are available. When used as insulation in electrical motors and generators, it increases their safe operating temperature, increases efficiency, and reduces fire hazards. When the coarser steam-blown fiber is gathered into a mat, it becomes a most useful heat insulator which is finding innumerable applications.

Fiberglas Mats. Fiberglas in mat or loose form is used as a heat insulator in houses, Pullman cars, battleships and submarines, refrigerators, and as a filter in air-conditioning. The fiber for this purpose resembles staple fiber but is of coarser texture. In many of these uses it is considered as one type of "mineral wool," a trade name which also includes wool made from rock or slag. These various products all have about the same thermal conductivity, but the presence of unfiberized material, shot and slugs cause the rock and slag wool to have a higher density, about 10 pounds per cubic foot. Glass wool has a natural density of about 1.5 pounds per cubic foot, and when compressed to 10 pounds has a lower conductivity. Figure 16 shows the thermal conductivity of glass wool of different density at various temperatures.

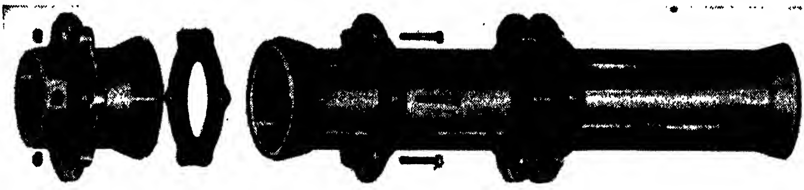

FIG. 17. Detail of Connection in "Pyrex" Glass Pipe. (Courtesy Corning Glass Works)

Rock Wool. The rock or slag wools are made by melting in a cupola, usually with coke as fuel. The molten charge is run into upwardly-directed jets of steam which shred it into wool. The raw product is of variable fiber-thickness, and contains from 10 to 30 per cent of granular material called "slugs," some of which is usually removed before marketing. The raw materials are of widely differing character: argillaceous limestone or calcareous shale, ordinary shales, lead, iron or copper slags. To these may be added limestone, dolemite or quartz rock to give a more easily melted mix. Rock and slag wools differ widely in composition, but a representative one is: SiO_2, 42 per cent; Al_2O_3, 12 per cent; CaO, 34 per cent; MgO, 10 per cent; Fe_2O_3, 1 per cent. When the lime content is too great the wool tends to disintegrate and settle from reaction with moisture, and the presence of sulfides also causes deterioration.

Building Blocks—The production of glass building blocks, a recent development, is now about two and a half million square feet per year. The glass must be of high chemical durability, and is usually of the soda-lime type containing alumina or boric oxide. The blocks are hollow, and are pressed in two parts. The molten glass is delivered in units or gobs of the proper size by an automatic feeder to an automatic press. The half-sections from the press are sealed together before cooling, either by dipping the edges in molten aluminum and pressing together, or by transferring the hot sections to an automatic sealing machine. This is a rotating and indexing machine which carries the hot sections over and above stationary burners, and then moves the hot sections into contact and presses the weld. The subsequent annealing of the rigid, entirely closed, and stressed blocks is difficult and requires special equipment designed to give the necessary time- and temperature-schedules which must be precisely followed.

TABLE 5—ESTIMATED WORLD PRODUCTION OF GLASS AND GLASS PRODUCTS*

(Values have been converted into U. S. Dollars)

Official Statistics Unless Otherwise Noted

Producing Country	*Year*	*—Production (000 omitted)—*		*No. of Establishments*	*Employment*
		Metric Tons	*Value (U.S. $)*		
United States......	1935	2,948 [3]	283,925	213	67,100
Germany.........	1935	700 [4]	132,400 [2]	300 [6]	85,100 [10]
United Kingdom...	1934	775 [8]	76,000	125 [6]	43,000
Rumania..........	1930	500 [3]	40,000 [7]	63 [3]	6,000 [3]
Czecho-Slovakia...	1935	148 [1]	29,000 [1]	200	22,000 [9]
France............	1937	476 [3]	28,000 [3]	147 [3]	38,000 [3]
Belgium..........	1935	235 [1]	25,000	125 [6]	28,500 [3]
Italy.............	1935	100 [4]	25,000	500	28,000 [3]
Japan............	1935	500 [3]	20,000	696	23,866
Soviet Russia......	1935	600	11,000 [11]	....	71,000
Canada...........	1935	75 [8]	10,000	68	3,100
Sweden...........	1935	65	7,156	58	5,000
Australia..........	1937	85 [7]	7,000 [3]	3	4,000 [3]
Poland...........	1935	97	6,000	60	10,000
Netherlands.......	1935	75 [3]	5,000 [3]	10 [3]	5,000 [3]
Yugoslavia........	1931	45 [3]	3,500 [3]	6 [3]	1,500 [3]
Denmark.........	1935	25 [8]	2,000	5	1,163
Norway..........	1936	12	1,350	5	855
China............	1933	15 [3]	1,144 [3]	40 [3]	4,000 [3]
Spain.............	1935	30 [5]	1,000 [5]	150 [3]	([12])
Portugal..........	1935	10 [3]	1,000 [3]	7 [3]	([12])
Austria...........	1926	10 [5]	4,000 [5]	10 [3]	2,500 [3]
Latin America.....	1935	100 [3]	11,000 [3]	105	17,000 [3]
Total (estimated)..		8,000	800,000	3,000	500,000

Basis of estimates:

[1] Known relationship to exports.

[2] Fuel activity in relation to previously compiled data.

[3] Trade estimates.

[4] Value per ton as indicated by exports.

[5] Known relationship to imports.

[6] Lists of manufacturers.

[7] Metric ton valued at $80.

[8] 140 per cent of sand consumption.

[9] 54 per cent of average (40,000).

[10] 85 per cent of 1928 total.

[11] Unofficial domestic rate of ruble $.03.

[12] No basis for estimate.

* From "World Production and Trade in Glass"—Bureau of Foreign and Domestic Commerce, U. S. Dept. of Commerce.

Chemical Engineering Construction—During the past 15 years glass has been increasingly used in chemical engineering construction where corrosion is troublesome or where purity of product is essential. Used originally in the heavy-chemicals industry, particularly against HCl solutions or wet chlorine gases, it has more recently found numerous practical applications in processing fine chemicals, pharmaceuticals, foods and beverages. "PYREX" glass piping of heat and chemical resistant glass, complete with fittings and accessories, is available in sizes up to 4" I.D. and is designed for maximum working pressures of 100 pounds per square inch. Figure 17 shows the construction of the special pipe joint. Other glass chemical engineering equipment includes heat-exchangers, bubble-towers, absorption columns, raschig rings, and centrifugal pumps.

THE ECONOMICS OF THE GLASS INDUSTRY

The first attempt to obtain a world-wide statistical picture of the glass industry is given in Table 5, reprinted, with revision, from Morey.[19] The data represent conditions before the outbreak of war in 1939; present conditions are too unsettled for estimates to be of value and future trends are unpredictable. The most significant fact brought out is the pre-eminent position of the United States as a consumer of glass. The production of glass in the United States is ⅜ of the total world production, four times that of either of the two nearest competitors, the United Kingdom or Germany, and three times the total of Germany, Austria and Czecho-Slovakia. The glass exported from the United States (Table 6) is only one-seventh that from Germany, one-tenth that exported from Germany, Austria and Czecho-Slovakia. From these data it follows that the United States' market for glass is almost equal to that of the rest of the world, and the consumption per capita is more than twice that of any other country. Exports of glass from the United States first exceeded imports in 1933, and in 1939 the total value of imports was $5,156,000; of exports, $10,422,000.

TABLE 6—EXPORTS OF GLASS FROM PRINCIPAL COUNTRIES OF PRODUCTION*

(Values converted into U. S. $1000)

Country of Export	*1929*	*Per Cent of Total World's Exports*	*1936*	*Per Cent of Total World's Exports*	*Approximate Per Cent of Local Production*	*1938*	*Per Cent of Total World's Exports*
Germany	61,300	29	55,387	41	40	33,438	32
Czecho-Slovakia	40,804	20	24,138	18	80	17,805 [1]	17
Belgium	42,023	21	18,641	14	75	17,034	16
United States	10,931	5	8,264	6	3	8,332	8
United Kingdom	11,000	5	7,800	6	10	7,884	8
Japan	6,090	3	7,438	5	40	7,365	7
France	21,281	10	5,870	4	20	5,308	5
Austria	2,287	1	2,187	2	50	1,846 [2]	2
Netherlands	3,557	2	1,742	1	35	1,739	2
Italy	2,032	1	1,109	1	4	2,094	2
Sweden	1,221	..	1,062	1	14	1,149	1
U. S. S. R.	2,200	1	720	..	6	571	1
China	600	..	372	..	30		
Australia	175	..	320	..	5		
Others (estimated)	1,765	.	450				
Total (estimated)	205,000	..	135,500				

[1] First nine months.

[2] First ten months.

* Bureau of Foreign and Domestic Commerce, U. S. Dept. of Commerce.

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[19] Morey, G. W., "Properties of Glass," Reinhold Publishing Corp., New York (1938).

TABLE 7—UNITED STATES FOREIGN TRADE IN GLASS*

United States Imports and Exports of Glass and Glass Products

(Values in thousands of dollars)

Country of Origin or Destination	*1900*	*1920*	*1929*	*1933*	*1937*	*1938*	*1939*
IMPORTS							
Germany	1,464	1,869	4,357	1,558	2,487	1,780	1,748
Czecho-Slovakia	(1)	338	2,840	769	2,940	2,215	239
Belgium	1,687	1,893	2,733	204	1,202	611	964
Japan	3	308	178	134	1,022	547	587
France	639	612	2,097	320	428	377	436
United Kingdom	444	1,167	740	250	561	418	527
Italy	38	67	407	106	136	147	153
Netherlands	24	472	262	51	28	22	29
Sweden	3	26	159	22	127	139	199
All other	736	825	220	104	1,241	272	274
Total	5,038	7,577	13,993	3,518	10,172	6,528	5,156
TYPE OF WARE							
Window glass	2,099	623	2,184	161	1,504	834	793
Plate glass	247	2,271	2,256	140	738	115	75
Containers	464	305	308	644	719	566	383
Household glassware	(1)	(1)	282	1,464	4,202	3,091	2,715
Other glassware	2,228	4,379	8,963	1,109	3,009	1,922	1,190

Country of Origin or Destination	*1900*	*1920*	*1929*	*1933*	*1937*	*1938*	*1939*
EXPORTS							
Canada	580	7,964	5,068	1,998	4,288	3,608	4,615
Cuba	167	5,296	1,083	311	1,652	1,180	1,311
Philippine Islands	6	590	340	200	339	423	570
Mexico	282	2,191	580	261	591	342	528
Union of South Africa	17	348	159	80	326	326	423
Australia	249	861	323	250	242	302	360
Colombia	13	575	193	49	269	251	411
United Kingdom	141	4,258	483	110	334	248	250
Venezuela	5	402	83	19	193	247	322
Panama	(1)	319	139	91	240	217	237
All others	476	7,872	2,480	936	1,310	1,188	1,395
Total	1,936	30,776	10,931	4,305	9,784	8,332	10,422
TYPE OF WARE							
Window glass	36	4,097	605	154	53	36	194
Plate glass	(1)	2,854	745	1,170	984	791	1,106
Glass containers	(1)	9,576	3,570	1,116	3,321	2,896	3,454
Table glassware	(1)	423	1,658	424	1,750	1,581	1,963
All other	1,900	13,136	4,353	1,441	3,676	3,028	3,705

[1] Data not shown separately.

* Bureau of Foreign and Domestic Commerce, Dept. of Commerce, Washington, D. C.

Employment in Glass Industry—Another significant comparison is that of employment in the industry. In 1935 the United States produced 2,948,000 tons of glass with an employment of 67,100, or 43.9 tons per person. Germany, with a production of 700,000 tons, less than a quarter that of the United States, had

TABLE 8—GENERAL STATISTICS OF THE GLASS INDUSTRY OF THE UNITED STATES, 1931-1939[*]

	1931	*1933*	*1935*	*1937*	*1939*
Number of establishments	229	213	213	232	229
Salaried personnel[1]	....	....	6,212	7,956	7,316
Salaries[1, 2]	....	....	$ 14,384,855	$ 17,803,799	$ 17,285,000
Wage earners[3]	49,917	49,797	67,138	75,051	69,821
Wages[2,3]	$ 57,881,550	$ 45,221,754	$ 71,443,178	$101,597,694	$ 88,304,912
Cost of materials, etc.[2]	73,574,568	63,409,894	110,040,997	140,705,050	120,775,400
Value of products[2]	216,264,830	191,947,716	283,925,061	387,709,563	357,978,022
Value added by manufacture[4]	142,690,262	128,537,822	173,884,064	247,004,513	237,202,622

[1] No data for employees of central administrative offices are included.

[2] Profits and losses cannot be calculated from the census figures because no data are collected for certain expense items, such as interest, rent, depreciation, taxes, insurance and advertising.

[3] The item for wage earners is an average of the numbers reported for the several months of the year and includes both full-time and part-time workers. The quotient obtained by dividing the amount of wages by the average number of wage earners should not, therefore, be accepted as representing the average wage received by full-time workers.

[4] Value of products less cost of materials, supplies, fuel, purchased electrical energy and contract work.

[*] Bureau of the Census, Department of Commerce, Washington, D. C.

TABLE 9—STATISTICS OF THE GLASS INDUSTRY OF THE UNITED STATES, 1939[*]

Flat Glass	*Value*
Window glass	$ 24,326,040
Obscured, including cathedral and opalescent	2,235,080
Wire glass, rough and polished	2,291,800
Other flat glass[1]	42,532,677
Total flat glass	$ 71,385,597
Container Glass	
Food product containers	$ 60,185,027
Beverage containers	51,218,689
Medicinal and toilet containers	38,171,646
General purpose and not classified	6,789,475
Total containers	$156,364,837
Tableware, Pressed and Blown Glass, and Not Otherwise Classified	
Machine made (automatic) tableware	$ 28,366,098
Hand made tableware	11,655,462
Lighting glassware	21,484,048
Lenses[2]	2,116,938
Technical, scientific and industrial glass	9,952,699
Pressed and blown glassware[3]	19,079,573

[1] Includes polished plate, other safety glass (not laminated), rough plate glass and spectacle glass.

[2] So-called lenses for use in headlights, lighthouses, lanterns, etc. Optical glass lenses not included.

[3] Includes glass cooking ware or ovenware, fiber glass products, building glass not otherwise classified, pressed specialties, etc.

[*] Bureau of the Census, Department of Commerce, Washington, D. C.

an employment of 85,100, almost one-quarter greater, or 8.2 tons per person. The total of Germany, Austria and Czecho-Slovakia gives a production of 7.9 tons per person. These differences in productivity offer striking evidence of the tendency of American manufacturers to develop mass production [20] methods.

In 1937 the glass industry of the United States was 24th [21] in order of industries based on number of wage earners, and 38th in value of product. Its rank in value added in manufacture [22] was 25th; but of the first 25 industries it was fourth in ratio of value added in manufacture to total value of product. In this respect it is exceeded only by the printing and publishing industries, and by foundry products. In 1939 the total value of the glassware produced in the United States was $320,405,252, produced by 69,821 manufacturing wage earners.

International Trade—Table 7 gives a survey of world trade in glass, and shows the source and amount of imports and exports into the United States, and destination and amount of exports. Prior to 1939, Germany and Czecho-Slovakia were the source of more than half of our importations of varied types of ware. The importations from Belgium have been largely of flat glass. Our most important export market for many years has been the Canadian-Newfoundland area. Latin America is second, with largest shipments going to Cuba, Mexico, Colombia, Venezuela and Panama. In 1937, of a total importation into Latin America of 13.5 million dollars, 4.0 million, or 29 per cent, came from Germany; 3.3 million, or 25 per cent, from the United States; Belgium, 22 per cent; Czecho-Slovakia, 10 per cent; the United Kingdom, 5 per cent; and Japan, 3 per cent. In 1935 the United States was the leading exporter of glass to Latin America, obtaining 25 per cent of the business, while Germany was second with 24 per cent. Flat glass is the leading type of glass product being imported by Latin America, amounting to 37 per cent of the total. Glass containers were next in value, 25 per cent of the total, and household glassware accounted for 16 per cent of the total importation. Next to Latin America comes the Far East, largely because of sales to the Philippine Islands.

Table 8 gives general statistics for the industry as a whole, and in Table 9 this is broken up into different sections by product.

READING LIST

GLASS MANUFACTURE

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Hodkin, F. W. and Cousen, A., "A Textbook of Glass Technology," Constable & Co., Ltd., London (1925).

Rosenhain, W., "Glass Manufacture," second edition, Constable & Co., Ltd., London (1919).

Scholes, S. R., "Modern Glass Practice," Industrial Publications, Inc., Chicago (1935).

Scholes, S. R., "Handbook of the Glass Industry," The Glass Industry, New York (1941).

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[20] See Chapter 1, "The Economic Pattern."

[21] Bureau of the Census, Dept. of Commerce, Census of Manufactures, 1937 (July 8, 1937).

[22] The "Value added in manufacture" is used by the Bureau of the Census as the most satisfactory measure of the importance of an industry. It is the difference in cost of raw materials, including fuel and power, from the value of finished product.

PROPERTIES OF GLASS

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PHASE DIAGRAMS

Findlay, A., "The Phase Rule and Its Applications," 7th Ed., Longmans, Green & Co., New York (1931).

CHAPTER 21

THE CLAY PRODUCTS INDUSTRIES

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The clay products industry is one of the oldest of the manufacturing industries. Primitive clay vessels were merely sun-baked, and therefore very limited in their uses, but very early man learned that if clay vessels are heated to a red heat in a fire their strength is greatly increased and that the clay no longer softens in water. During the centuries that followed, the utility and desirability of clay wares was appreciated more fully, and clay was used in the manufacture of a larger variety of articles. With the introduction of Portlant cement, a serious competitor started to replace clay products in a number of instances, and since then newer materials of construction threaten to compete more seriously with a variety of clay products. However, clay products possess certain desirable properties so that the industry as a whole is quite secure. In favor of clay wares should be mentioned abundant and cheap raw materials. The highest price for best quality refined clay seldom is above $20.00 a ton, the average price of all domestic clays being under $5.00 a ton. Clay wares also possess durability and beauty that has not been successfully imitated.

Scope of the Industry[1]—Clay products of one type or another are made in every state of the Union. Considering the value of all clay products produced, Ohio has been the leading producing state, but in the past several years Pennsylvania has practically equaled Ohio, each producing approximately 20 per cent of the total U. S. production, New Jersey, West Virginia, California and Missouri following in order.

The value of all clay products produced in the U. S. in 1899 was 96 million dollars; this increased steadily until 1926 when the total value was approximately 460 million dollars, followed by a decline to 97 million dollars in 1932, followed again by a rise to 155 million dollars in 1935, dropping again to 109 million dollars. These data indicate that clay products suffer from competition of other materials and are hard-hit in times of economic depression, but that there is a basic, stable demand amounting to something over 100 million dollars annually.

Heavy-clay products production suffered severely during the depression. Common brick production reached a maximum of 7.6 billion bricks in 1925, then declined approximately 1 billion in 1932, followed by another maximum of a little over 3 billion in 1937. The trend in face bricks has been similar, with ap-

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[1] For reference to statistical information, see bibliography at end of chapter. Information on location, importance and development of the industry is ably presented by Hamilton, C. A., "Marketing Burned-Clay Products," The Ohio State University Columbus, Ohio (1939).

proximately 2.5 billion bricks produced in 1924. Paving brick production was at its maximum in 1914 after which it declined fairly regularly until 1933 when it was down to about 200 million bricks, and has stayed near that figure since. Concrete and bitumen mixes have been largely responsible for the decline for demand for paving bricks.

Total pottery production reached a maximum of approximately 118 million dollars in 1924, then declined to a low of 53 million dollars in 1932.

The total clay products produced annually represents approximately one per cent of the value of all manufactured products.

CLAY, THE BASIC RAW MATERIAL

Nature and Origin—Clays vary widely in chemical composition and physical properties. They are mixtures of various minerals, but the basic constituents *kaolinite* ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) or similar hydrous aluminosilicates are common to nearly all clays.[2] Clays are the decomposition product formed by the weathering of feldspar or of feldspathic rocks; the following reaction is usually given as typical:

$$\underset{\text{(Orthoclase feldspar)}}{K_2O \cdot Al_2O_3 \cdot 6SiO_2} + CO_2 + 2H_2O = \underset{\text{(Kaolinite)}}{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O} + \underset{\text{(Sand)}}{4SiO_2} + K_2CO_3$$

The soluble potassium carbonate is leached away but the sand and other insoluble minerals are left mixed with the kaolinite, and the combined deposit is called clay.

If the clay thus formed is found overlying the parent rock it is termed *residual* or *primary* clay; if the clay has been carried to other regions by currents of air, water or by glaciers it is called *sedimentary* or *secondary* clay.

Residual clays are mixtures of kaolinite or related hydrous aluminosilicates, sand and undecomposed particles of the parent rock. As a rule, the farther down one digs through a residual clay deposit, the greater the admixture of undecomposed parent rock, until finally the original rock mass is encountered. If this deposit contains little or no iron, it is called *kaolin, kaolin rock* or *china-clay rock.* The undecomposed rock particles and sand can be removed by a washing process leaving a clay high in the mineral *kaolinite*; such a washed clay is called *china clay* and is an important constituent in whitewares. All china clay imported from England is derived from residual kaolins. Domestic kaolins are obtained mainly from western North Carolina, but smaller amounts are also obtained from Pennsylvania and New Jersey.

Sedimentary clays are usually of a finer texture than the primary clays, for the coarser mineral particles have dropped out in transit. The deposits can be recognized by their stratification and the clays usually bear no relation to the underlying rock. A sedimentary clay may therefore have undergone a washing or purifying process during transit and thus be considerably purer than the parent residual clay. However, as has happened much more frequently, impure clays and other sediments are also transported to the same deposit and mixed with the purer clay so that the net result is a relatively impure clay. This process of

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[2] For a fuller discussion of the nature of clay see Kerr, P. F., Jour. A. Cer. Soc., *21*, 267-286 (1938).

transportation is going on at the present time just as it has for ages past, and it can readily be seen that the red and brown muddy waters seen at times in nearly all streams, will, when they deposit their burden at their final resting place, add nothing to the purity of the deposit. Clays that have been deposited in their washed and purified form in the past, without addition of other impurities, are indeed rare. Outstanding examples of fairly pure sedimentary clays are the ball clays of western Kentucky and Tennessee, the white-burning clays of Georgia and South Carolina and the plastic kaolins of Florida. Many sedimentary clays are plastic and white burning and are therefore also classed as china clays, and in commercial circles sometimes as kaolins.

Sedimentary clays comprise a large group of clays having great variations in their properties. This classification includes clays used for face bricks, common bricks, fire bricks, stoneware, terra-cotta, roofing tile and also includes soil clays.

Sedimentary clays are often covered to great depths by other sediments so that they are subjected to great pressures, which cause them to form into firm masses called shale. If the clay particles in shale have not been surrounded by deposited mineral matter, they will, on grinding, develop plasticity when mixed with water. If in addition to the intense pressure the shales are subjected to heat, they may lose a good share of their chemically combined water, thus being transformed into slate and schist.

Chemical Composition—The kind and amounts of minerals in a clay determine to a large extent its suitability for any particular purpose, but the physical states of the minerals also have an important bearing on their usefulness. In the chemical analysis of clays, the various constituents are usually reported as the oxides; such an analysis is called an ultimate analysis and is of considerable aid in forecasting the suitability of a clay for certain purposes. The average ultimate analyses of various clays, compiled from Ries,[3] are given in Table 1.

TABLE 1—ULTIMATE ANALYSES OF VARIOUS CLAYS

	SiO_2	Al_2O_3	FeO, Fe_2O_3	CaO	MgO	Na_2O, K_2O	TiO_2	*Ignition Loss*
Kaolin	57.84	28.66	0.91	0.18	0.32	0.80	0.0	10.37
Ball-clay	48.61	35.38	0.98	0.39	0.31	2.12	0.50	11.56
Fire-clay	60.75	25.56	1.36	0.29	0.35	1.23	0.96	9.39
Stoneware clay	58.09	20.79	2.48	0.32	0.74	1.67	0.48	7.60
Sewerpipe clay	58.84	21.34	6.12	0.47	1.00	3.42	0.38	0.68
Paving-brick clay	56.00	22.50	6.70	1.20	1.40	3.70	...	7.00
Common-brick clay ...	58.00	13.60	4.17	6.92	1.35	3.33	0.40	11.36

Many ceramists find more use for a rational analysis, which indicates the amount of different mineral constituents present. The minerals in a high grade kaolin consist chiefly of kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, orthoclase feldspar, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, and quartz, SiO_2. Each of these minerals exerts its influence on the properties of the clay: the kaolinite is plastic and refractory; the feldspar is non-plastic and easily fusible; the quartz is non-plastic and reduces the shrinkage due to kaolin and feldspar. It is therefore desirable that for certain purposes the constituents be held within close limits. A rational analysis helps the clay

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[3] Ries, H., "Clays, Their Occurrence, Properties and Uses," third edition, John Wiley & Sons, Inc. (1927).

worker in adjusting the various clays by adding feldspar or sand or both in order to bring about certain desired properties.

A rational analysis can best be made with a petrographic microscope supplemented by an ultimate analysis. An approximate rational analysis can be calculated from an ultimate analysis, and methods have also been suggested for determining the rational analysis directly by chemical means.[4]

Mistakes can easily be made by judging a clay solely by its chemical analysis. Materials differing so widely in their properties as kaolin, ball clay and coal ash may have practically identical compositions as far as their ultimate analyses will show.

Impurities. In addition to kaolinite, clays contain various other chemical components which are usually classed as impurities, even though they confer very desirable properties to the clay. Free silica as quartz, SiO_2, is present in all clays and is also in the combined form in other minerals in the clay. It increases the refractoriness of clay at low temperatures, and even at high temperatures, if present in large quantities. It diminishes the air- and fire-shrinkage and increases the porosity of the fired product. Alumina, Al_2O_3, like quartz, is present in the combined form in kaolinite, feldspar, micas, and other minerals; it is a refractory component of clay. Iron oxide, FeO, Fe_2O_3, lime, CaO, magnesia, MgO, and the alkalies, K_2O, Na_2O, are classed as fluxes. They lower the fusion point of the clay, which is desirable for certain purposes, but is especially undesirable if the clay is to be made into refractory ware. The iron oxides are the strongest naturally occurring coloring ingredients in clay.

Clays with an iron oxide content up to a little over 1 per cent may burn white; buff-burning clays have an iron oxide content ranging from 0.5 to 5 per cent, and red-burning clays 4 to above 7 per cent. It will be seen from this that the color produced by iron oxide is not merely dependent on its amount; its physical state and other materials present, influence the color as well. For instance, lime, CaO, has a bleaching action on iron oxide. If iron is present in the clay in the ferrous state it is changed to the ferric state by the usual oxidizing conditions in the kiln. It may be possible, however, that so much carbonaceous material will be present that the oxidation is not completed by the time vitrification sets in, in which case dark colors are obtained instead of a red.

Lime is the cause of considerable trouble in the firing of clays; not only is it an active flux, but it gives a very short vitrification range to the clay, which may mean a large percentage of spoilage in the product of the kiln. If lime is present in the clay as carbonate it will burn to the oxide and may slake later; an expansion accompanies the slaking which is often sufficient to rupture the fired ware. If lime is present as sulfate it may cause efflorescence. Magnesia is not as objectionable as lime, for it gives a longer vitrification range to the clay than the lime does. It is sometimes added to clay to be used for paving bricks, producing a more uniform, tough product. The alkalies are the strongest fluxing ingredients in clay. They are present in the feldspars and micas. It is on account of the alkalies in clay that a relatively low-firing temperature produces the proper degree of vitrification. Feldspar is added to clays for certain wares to lower

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[4] For methods of analyses of clays see Ries, loc. cit., pp. 105-111, and J. Am. Cer Soc., *11,* 351-77 (1928).

the fusion point of the clay. Alkalies are undesirable in clays to be used for refractories. Mica is common to many clays, but if not present above 2 per cent it exerts but little influence on the properties of the clay.

Physical Properties—More important to many ceramists than the chemical properties of clays are their physical properties. A very important physical property is that of plasticity. Most clays when wet are plastic; i.e., they will yield under pressure and will hold the new shape when the pressure is released. The degree of plasticity varies widely in the different clays. The kaolins are but slightly plastic (lean) while the ball clays are very plastic (fat) but the difference in plasticity cannot be attributed to difference in chemical composition. If a clay is too plastic, its plasticity can be reduced by adding a less plastic clay or sand, while plasticity of a clay batch can be increased by adding a highly plastic clay. The plastic clays will take up more water than the less plastic ones and on drying will, therefore, be more subject to shrinking and cracking. The practical potter can readily tell by the "feel" whether a clay batch has the right degree of plasticity for his particular piece of work, but modern scientific developments require that the human element be eliminated as far as possible, and more precise methods for determining the degree of plasticity would be desirable. No satisfactory all-around method has yet been devised. Wilson[5] gives a review of various methods that have been used with some degree of success, and a summary of the theories proposed to account for the plasticity of clays.

Other important physical properties are texture (fineness) including distribution of sizes of particles, tensile strength, air- and fire-shrinkage, porosity and fusibility.

Types of Clays—Certain types of clays have well-recognized properties and have found special uses in the arts. In some cases a clay used for one purpose may also be used for some other, but the following types may be mentioned. A difficulty encountered here is that certain terms through long years of use have changed their meanings considerably or some terms have been used loosely without much regard to their original meaning.[6]

Kaolin. This term has been variously used to designate (1) A primary clay of low plasticity but with a high degree of purity, (2) Sedimentary white-burning plastic clays of Florida, (3) An amorphous variety of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (the crystalline form is called kaolinite), (4) China clay. A suitable present-day definition is: (5) A white-firing clay which in its beneficiated condition is made up chiefly of minerals of the kaolinite type.

China Clay. The term china clay can properly be applied to a relatively pure commercial variety of kaolin derived from the original kaolin formation by an artificial or, in some cases, a natural washing process. In this washing process, which may consist of elutriation, levigation or sedimentation, the disintegrated clay mass is agitated with a large amount of water and is then allowed to stand quietly in a pond or large tank. The coarse particles of sand, flint, mica and other parts of the undecomposed parent rock settle out in the washing process,

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[5] Wilson, H., "Ceramics, Clay Technology," pp. 107-119, McGraw-Hill Book Co., Inc. (1927).

[6] To remedy this lack of uniformity the Committee on Geological Surveys of the American Ceramic Society prepared a list of 58 definitions, which are published in Bull. Am. Ceram. Soc., *18*, 213-215 (1939).

leaving a relatively pure white-burning clay.[7] Kaolin and china clay are grouped together in government statistics. The clays are used for paper filler and coating, whiteware, refractories, and a variety of other purposes. Over three times as much china clay is used in the paper industry than is used in the clay products industries.

Georgia produces approximately two-thirds of the domestic kaolin with South Carolina and Pennsylvania following in order. Florida, although producing a relatively small tonnage, produces a high grade of plastic kaolin. An appreciable amount of china clay is imported from England.

Ball Clays. Ball clays are sedimentary clays and have a high degree of subdivision. They derive their name from the shape of the clay masses as they are dug from the deposits, first in somewhat cubical forms which become rounded with handling. On account of the extreme fineness of the particles[8] and because of some organic matter present, these clays are exceptionally plastic. They also have a high drying shrinkage and are relatively strong in the dry unfired state. The ball clays vitrify at lower temperatures than do china clays. Ball clays usually contain an appreciable amount of organic matter which burns out in the kiln leaving a white or cream mass. The organic material discolors the raw clay which leads to such names as blue ball clay and black ball clay. Ball clays mixed with china clay are used in a large number of whiteware bodies used for making dinnerware, electrical porcelain and wall and floor tile. Ball clays are mined in western Kentucky and Tennessee, with much smaller amounts in New Jersey; appreciable amounts are imported from England.

Fire Clays. Fire clays will stand a high degree of heat. As a rule clays are expected to withstand temperatures above 1600° C. (2912° F.) before they are classed as fire clays. In order to withstand such temperatures a clay must have a small percentage of fluxes, such as Fe_2O_3, FeO, CaO, MgO, K_2O, Na_2O and TiO_2. Usually the sum of all these fluxes represents less than 4 per cent of the total, and commonly less than 3 per cent. The SiO_2 content for regular fire clays ranges between 40 and 60 per cent and the alumina between 25 and 45 per cent. High alumina clays may contain Al_2O_3 above 70 per cent. The high alumina clays are obtained principally from Missouri and contain relatively large amounts of diaspore, $Al_2O_3 \cdot H_2O$. Such clays are highly refractory and are used for refractories intended for severe duty.

Fire clays are commonly divided into the following types: plastic clays are soft and easily worked into desired shapes; flint clays are hard and rock-like due to great pressures encountered since their deposition and require fine grinding to develop plasticity; refractory shales are fire clays that have been converted to shales as described in the following section. Fire clays are used for making refractory wares such as fire bricks, special shapes and muffles, but in some cases are also used for making structural wares such as face brick and hollow building tile.

Shales. These are clay strata that have become hardened by pressure and usually also by heat, but chemical alteration has not taken place. On exposure to weather they soften and become more clay-like and may become fairly plastic

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[7] Davidson, E. H., Ceram. Age, *32,* 74-5 (1935); Maddock, J. B., ibid., *33,* 12-4 (1939).

[8] Whittaker, H., Jour. Amer. Ceram. Soc., *22,* 16-23 (1939).

after wet grinding. Shales are widely used in the manufacture of structural clay products.

Buff and Red-Firing Clays. These clays, together with shales, form the basis of a large industry manufacturing what is commonly known as heavy clay products or structural ware. The red and dark firing clays contain some form of iron oxide together with other impurities and as a rule will not stand as high a temperature as the buff burning clays, and are widely used for face bricks, common bricks, and hollow tile. Buff-firing clays are also widely distributed, large quantities being found in the coal bearing seams of Pennsylvania, West Virginia and eastern Ohio. The hardness may vary from a shale-like variety to a soft plastic variety. The clays find use for making structural brick and tile, terra cotta, stoneware, sewer pipes and pottery.

DOMESTIC PRODUCTION, IMPORTS AND EXPORTS OF CLAYS

The total clay sold by producers in the United States has increased from year to year with some irregularities since 1929 and amounted to four million tons valued at 17 million dollars in 1939. Noticeable has been the increase in kaolin and china clay production, increasing steadily from 121,000 tons in 1905 to 780,800 tons in 1939. This increase is largely due to the improved quality of the clay produced. For a long time potters and paper makers felt that English china clay was necessary for their wares. English china clay had the advantage of being very uniform, and the consumers could depend on obtaining the same uniform quality year after year, and to the users this was an important advantage. The American deposits lack this uniformity. However, during the past decade the domestic producers have developed methods of purification and blending[9] under careful scientific control so that they can guarantee a high degree of purity and uniformity with the result that many potteries and paper factories now depend entirely upon the domestic supply. The consumers have likewise put their production on a more scientific basis and can now more readily cope with slight variations in the quality of the clays.

The domestic production of ball clay and of fire clay has not increased in the same proportion that china clay has, each approximately doubling in amount from 1905 to 1939.

The importation of clays increased steadily since 1900 until 1926 when nearly half a million tons were imported; since that year the trend has been downward; in 1939, 151,500 tons were imported, valued at one and a third million dollars. In addition to china clay importation, which in 1939 amounted to 116,000 tons, close to 30,000 tons of "common blue and Gross-Almerode" clays were imported. The common blue clay generally refers to English ball clay and Gross-Almerode, to a German refractory clay used in the manufacture of glass pots. Lesser amounts of fuller's earth and miscellaneous clays were also imported.

Statistics available[10] do not give a true picture of the total clay mined, for clays utilized for making bricks, sewer pipe and other heavy clay products are not

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[9] Grout, J. R., Jr., Bull. Amer. Ceram. Soc., *16*, 387-90 (1937).

[10] "Minerals Year Book" and "Mineral Resources of the United States," U. S. Bureau of Mines, both published annually, Superintendent of Documents.

included in the statistics, for they are ordinarily made into finished products by the producer.

The United States exports a relatively small amount of clay. Approximately 3½ per cent of the total clay mined and sold by producers is exported. Fire clay and fuller's earth are the chief exported clays.

CLAY PREPARATION

When clay is delivered to the plant it must be prepared for the process in which it will be used. The preparation consists of one or more steps which resolve themselves into a number of unit operations.

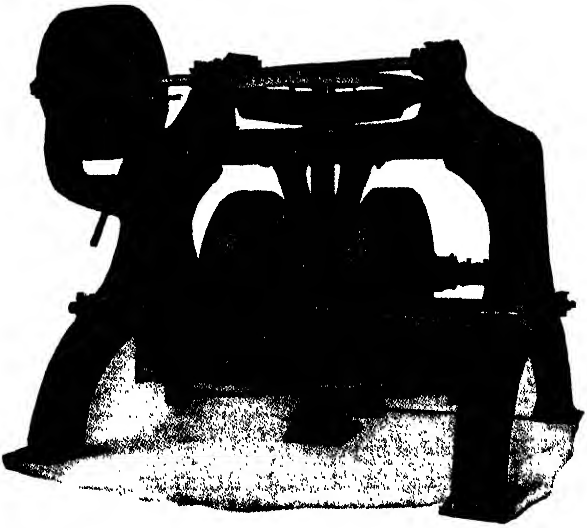

FIG. 1. Dry Pan.

Disintegration—Weathering improves all clays, but since it ties up capital for a considerable time it is not used to any large extent. The clay in layers 2 to 3 ft. thick is exposed to the action of rain, frost, and the sun for a period varying from a few months to several years. In the weathering process some of the soluble salts are leached out, the larger particles disintegrate through slaking, and the plasticity is improved. The process is necessarily expensive and more direct methods are usually used.

Shales and flint clays may require jaw crushers, but dry pans (Figure 1) are more commonly used. The pan rotates and as the material passes under the heavy wheels or mullers it is crushed. Centrifugal force throws the material over the perforated bottom to the rim of the pan, the fines falling through to the pit below. The scrapers then move the coarser material back under the mullers for further grinding. The clay and shale to be ground in a dry pan should be dry.

If the clay requires fine grinding, or if it contains small stones, roll crushers may be most satisfactory. Also in use are disintegrators for clay. A disintegrator consists of a large feed roll operated at a low rate of speed and a small disintegrating roll, which is provided with steel cutting bars, driven at a high rate of speed. The combination has the effect of removing successive portions of the clay, and at the same time breaking it up and destroying its original grain or fiber. Disintegrators will handle dry or damp clays. Ring roll crushers and hammer mills are finding wider application for fine grinding of clay and shales.

Prepared clay may be improved by aging the damp clay in a moist and dark room. Aging improves the plasticity of the clay because of bacterial growth. The action is believed to be due to some colloidal formation and due to removal of dissolved or entrapped oxygen in the clay. A poorly plastic clay will improve in its plastic properties in two days, but two weeks to several months is necessary for the maximum effect. Aging is not used as much as it was formerly, partly because the process ties up material in production for a considerable time, and de-airing processes, to be described later, in a number of instances obtain similar results in a few minutes.

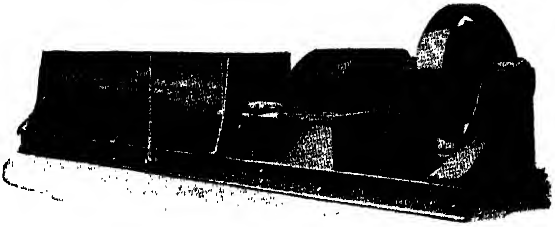

FIG. 2. Pug Mill.

Tempering—Plastic clays improve in their properties by tempering. This consists of thoroughly mixing the clay and the water content so that the clay becomes a uniform homogeneous mass throughout. Several machines have been developed for this purpose and in some cases grinding and tempering can be performed in a single operation.

Ring pits were formerly in common use and are still in use in some yards. The pits are about 25 ft. in diameter and from 2 to 3 ft. deep. A heavy wheel, usually of iron, is so arranged that it travels around the pit by horse power, in a spiral motion, thus grinding and mixing the clay.

Pug mills, Figure 2, are used in most modern plants. The mill consists usually of a horizontal semicylindrical tank, open at the top and containing longitudinally a rotating shaft to which are attached a number of blades set at different pitches. The blades work the clay into a homogeneous mixture and discharge the worked clay at one end. A pug mill takes up little room and power and is continuous in operation.

Wet pans also are used in modern plants for tempering and mixing clays. A wet pan is constructed similar to that of a dry pan except that it has a solid bottom. The wet pan is used for tempering clay or shale after it has been prepared in a dry pan or crusher preparatory to the manufacture of bricks and other heavy clay products.

The term "tempering" is also used in a different sense in connection with brick manufacture, in which case the term implies a partial and uniform reduction in the moisture content of bricks made by the soft-mud process.

De-Airing—If a plastic clay mass is subjected to a vacuum, a good deal of the dissolved and adsorbed air is removed from the clay. For many purposes this de-aired or evacuated clay has markedly improved properties over clay not so treated. De-airing may improve the plasticity, working, drying and firing properties of a clay. De-airing of a plastic clay mass is accomplished in a special de-airing machine, which consists essentially of two pug mills in tandem, with a vacuum chamber between. The first mill extrudes the clay in the form of flat ribbons into the vacuum chamber, where the air leaves the clay. The second mill compacts the evacuated clay into a solid mass and extrudes the clay in the customary bar or column. De-airing is applied to all types of clay products manufactured by the plastic method from heavy clay products, such as bricks, to the finest china bodies.[11] De-airing is also successfully applied to the manufacture of clay wares by the dry-press process and for preparing casting "slip." (See footnote 22, p. 841.)

Drying—In nearly all forming processes used in the clay industries, the wares after they are shaped, are in a damp condition. The moisture must be removed before the clay can be placed in the kiln for firing, for the rapid drying in the kiln would warp or crack the ware. In some instances the damp articles are merely exposed to the atmosphere until sufficiently dry, in others elaborate drying equipment is used with controlled temperature and humidity.

Shrinkage. Clays, like most porous materials, shrink on drying. In a wet clay, each tiny particle is surrounded by a film of moisture which holds the clay particles apart. As the moisture is removed by evaporation and these films are removed from the particles the latter are drawn closer together and the piece of clay shrinks. When the shrinkage has reached its maximum, there will still be free moisture in the pores throughout the clay, which is removed on further drying. The total moisture in clay is therefore divided into two groups, the shrinkage water, equal in volume to the total volume shrinkage of the clay on drying, and the pore water, equal to the difference between the total moisture content and the shrinkage water.

The amount of shrinkage of clay on drying will depend on the amount of moisture present and the nature of the clay. A ball clay, on account of the fineness of the particles, shrinks considerably, while a less plastic clay like a kaolin or a sandy clay, shrinks less. The linear drying shrinkage of clays varies from over 12 per cent down to a negligible amount. A clay with considerable amount of coarse material like sand may shrink very little. Sometimes fired clay is ground to form "grog" which is incorporated with the clay to reduce its drying shrinkage.

Drying Rates. Clay wares cannot dry uniformly throughout, for in order for the moisture to travel to the surface there must be a moisture gradient and the outside will be drier than the inside, and will therefore shrink first. During this time the damp and more plastic parts may yield to the distortion caused by uneven shrinkage, but by the time they dry and shrink the parts that dried earlier have lost their plasticity and have "set" so that permanent deformation and stress are bound to follow. This can be reduced by slow drying so that there

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[11] Garve, T. W., Bul. Am. Cer. Soc., *15*, **335-40 (1936)**; Kriegel, W. W., ibid., *12*, **338-40 (1933)**.

never is a great moisture differential throughout the ware. In massive clay articles like some terra-cotta pieces great care must be used during the drying process. In articles with thin sections only, like tea cups, such care is not necessary.

There are two essential factors in drying: rate of evaporation from the surface, which is governed by the temperature, humidity and velocity of the drying air; and rate of diffusion of the moisture through the material being dried, which depends upon the amount of moisture, the moisture gradient, the temperature of the material and the size and shape of the pores.[12]

The drying rate is accelerated at elevated temperatures because the rate of evaporation from the surface is increased, and the viscosity of the pore moisture is decreased so that diffusion from the interior to the surface takes place more readily. At higher temperatures there is danger that the surface moisture is removed too rapidly, causing an excessive moisture gradient through the ware and therefore uneven shrinkage with the possibility of cracks forming at the surface. The practical upper temperature limit for drying is about 90° C. (194° F.). In clay wares the limiting factor in the rate of drying is the diffusion rate of the moisture. Therefore, to increase this rate it is desirable to operate near the upper temperature range, but it is necessary to keep the air velocity low and the humidity high to prevent too rapid evaporation from the surface.

Types of Dryers. The oldest method of drying which is still in use is to place bricks out in the open to be dried by the sun and wind; sometimes the drying areas are covered with a roof. Drying sheds are also common in which the bricks are placed on boards which are held in tiers by racks. The sheds are more economical in space but are also limited to summer use.

Hot floors are used considerably for drying refractories. The floors may be heated by waste heat from the kilns or by direct heat from coal or oil fires, the hot gasses passing under the floor in flues, or the floors can be heated by steam pipes placed under the floor. On account of closer control of temperature and heat distribution, steam is preferable to other means of heating.

Tunnel dryers are widely used in the brick industry. The bricks loaded on cars are passed through heated tunnels, entering at the cool end and progressing slowly to the heated end as car after car is pushed into the tunnel on a predetermined schedule. For every car of moist bricks entering the tunnel a car of dry bricks leaves it. The tunnels are heated by direct firing in flues beneath the tunnels, by steam coils or by waste heat from kilns that are cooling.

In a newer development of the tunnel dryer, the tunnel is divided into sections, each section being under independent temperature and humidity control. In one dryer, for example, there are four sections separated by doors, each section containing four cars of clay wares. Periodically all doors open, including the end doors of the tunnel, and four cars of moist wares are pushed into the dryer at the cool end and four leave at the hot end. Each group of four cars advances to a new section of the dryer under a higher temperature and lower humidity than the preceding section. Circulating fans or injectors are used to circulate the air around the steam coils and through the bricks. This type of dryer is used for a variety of clay products, including structural wares and sanitary ware.

For drying tableware and electrical porcelain it has been common practice

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[12] For a discussion of the principles of drying, see Chapter 2.

to place the damp ware in a room heated with steam coils. A newer method, now widely used, is to use scientifically designed dryers that contain a set of conveyors. The ware to be dried is placed on boards which are placed in the dryers. The conveyor carries these boards up and down over pulleys, gradually moving the boards forward to the other end of the dryer, the boards with their load of wares always being kept horizontal. The specially constructed chamber in which this conveyor operates is heated with steam coils, and humidity control can be installed if desired. The drying time for dinnerware is usually under two hours.

FIRING

Firing is one of the chief steps in producing clay wares, for the firing process gives the clay its strength, hardness, durability and pleasing appearance. In all cases the clay is heated to a red heat or higher. Seldom can a clay be fired sufficiently hard at a temperature below 800° C. (1472° F.), while some wares like fire bricks may require a temperature of 1500° C. (2732° F.).

TABLE 2—FIRING TEMPERATURES OF VARIOUS CERAMIC MATERIALS

	Cone	° *C.*	° *F.*
Common brick	012-06	875-1015	1787-1858
Vitrified brick	5-10	1205-1305	2200-2381
Firebrick	5-18	1205-1490	2200-2714
Hollow blocks and fireproofing	03-1	1115-1160	2039-2120
Terra-cotta	010-8	895-1260	1643-2300
Red earthenware	010-05	895-1040	1643-1904
Sewer pipe	1-11	1160-1325	2120-2418
Vitreous floor tile	8-12	1260-1335	2300-2435
Stoneware	6-8	1230-1260	2246-2300
Semivitreous tableware, bisque	8-10	1260-1305	2300-2381
Semivitreous tableware, glost	4-7	1190-1250	2174-2282
Whiteware, overglaze decorations	019-010	660-895	1220-1643
Vitrified hotel china, bisque	11	1325	2418
Vitrified hotel china, glost	5-8	1205-1260	2200-2300

STAGES DURING FIRING

The firing of clay wares takes place in several stages, none of which, however, is definitely divided from a preceding or following stage. The stages or periods are commonly divided as follows:

1. Dehydration
    - (a) Mechanical dehydration or "water smoking" 20°-150° C. (68°-300° F.)
    - (b) Chemical dehydration or "chemical water smoking" 150°-600° C. (300°-1110° F.)
2. Oxidation, 300°-950° C. (570°-1740° F.)
3. Vitrification, 900° C. (1650° F.) and above.

Dehydration—During the dehydration period, water not removed during the drying process, and hygroscopic water adsorbed from the atmosphere are removed. In addition to this mechanical water, chemically combined water is also removed, as for instance that of the kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The greatest rate of moisture removal is near 500° C. (932° F.). Just following the chemical dehydration, the clay ware is at its greatest porosity. The time of water-smoking for bricks varies according to the moisture content, ranging from about twelve hours as a minimum to eight or ten days or even more for dry-pressed bricks which have not been previously dried. Low fires and a good draft to carry off the water vapor are ideal, but it is difficult to obtain a good draft with low fires. It is desirable to connect several kilns to one chimney so that a kiln under full fire aids in the draft of a kiln in the water-smoking stage. During this stage moisture and soot have a tendency to condense in the cooler parts of the kiln.

Oxidation—The oxidation period starts with the oxidation of the easily ignited organic matter at about 300° C. (572° F.) or less, and may continue up to above 900° C. (1652° F.). During this period the ferrous iron is changed to ferric iron, but before this can be completed the carbon must be oxidized, and prior to this, the sulfur must be oxidized. In other words, the more easily oxidizable sulfur and carbon must be removed before the bright-red of ferric oxide can be obtained, and all this must take place before vitrification begins. During this stage calcium and magnesium carbonates dissociate into their respective oxides and carbon dioxide.

Vitrification—The vitrification period is the period during which some of the minerals melt to a glassy state and on cooling bond the unmelted particles into a firm mass. For some wares, like high tension electrical insulators, vitrification is carried out to completion so that no pore spaces remain. During this stage the clay wares shrink and the amount of shrinkage is often taken as a measure of the progress of the firing. The vitrification temperature varies according to the sand and fluxes in the clay; for common clay the range is between 950° and 1050° C. (1742° and 1922° F.). The degree of vitrification obtained depends upon the temperature and the time (soaking period), while the degree of vitrification desired depends upon the nature of the wares fired. In common bricks complete vitrification is unnecessary, as a porous structure is not undesirable; paving bricks are more completely vitrified and are classed as vitrified bricks.

Coloration or Flashing—By shutting off the air supply from the fires the kiln atmosphere can be made strongly reducing, which if properly controlled may produce a variety of colors in the bricks. A clay that will ordinarily fire red (due to ferric oxide) will flash to brown due to the iron being reduced. Clays that burn buff in ordinary firing will change to a rich yellow or brown during the flashing period.

Cooling and Annealing—All clayware should be cooled slowly in the kiln after the temperature is down to a low red heat; then all drafts are shut off completely so that the ware may be annealed properly. If the annealing is not carried out carefully, strains will develop in the bricks or other wares fired in the kiln, which diminishes their soundness and toughness. Cooling cracks may be so small as to escape casual observation, but can be detected by the lack of the ring when two bricks are struck together.

Kilns—Various types of kilns for firing bricks, pottery and clay wares in general are in use. They vary widely in construction and operation and do not admit of simple classification, but the following types of kilns exemplify the chief ones in use today.

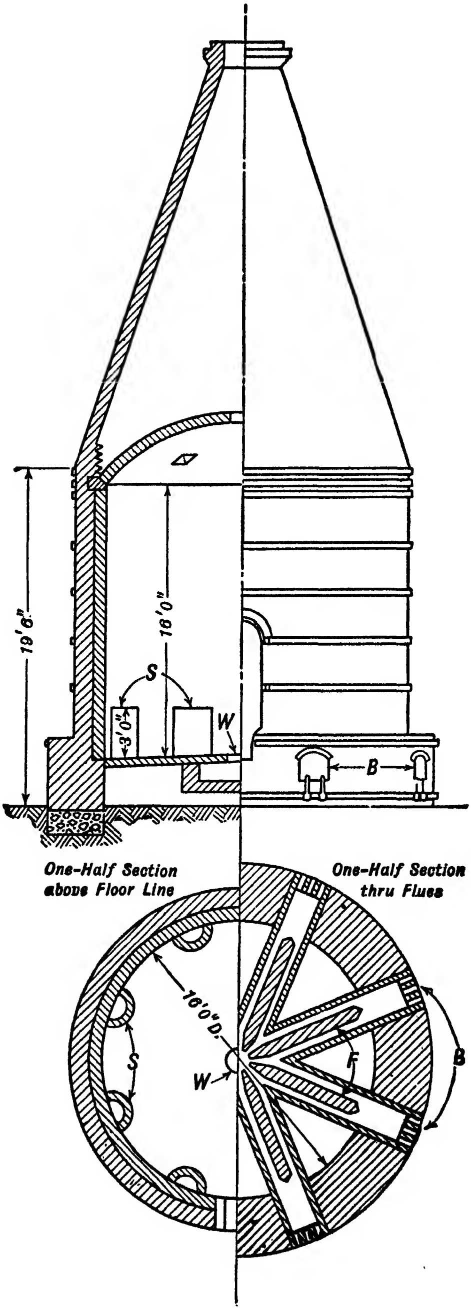

FIG. 3. An Up-draft Periodic Pottery Kiln.

Scove-Kiln. One of the oldest types of kilns for firing bricks is the "scove-kiln" or "clamp," which is an intermittent up-draft, open top, and open-fire kiln. The bricks are set in the form of large rectangular blocks about forty courses high, so arranged that fires may be built in openings left at the bottom and that the products of combustion can pass upward through the brick setting. The bricks are surrounded by temporary brick walls daubed on the outside with clay to keep the heat in and to keep drafts out. The top is covered closely with a layer of bricks and any sections showing local heating on account of localized drafts are covered with dirt to check the draft. Such a kiln is easy to construct but is of a temporary nature. This type of kiln is used mainly for firing common bricks.

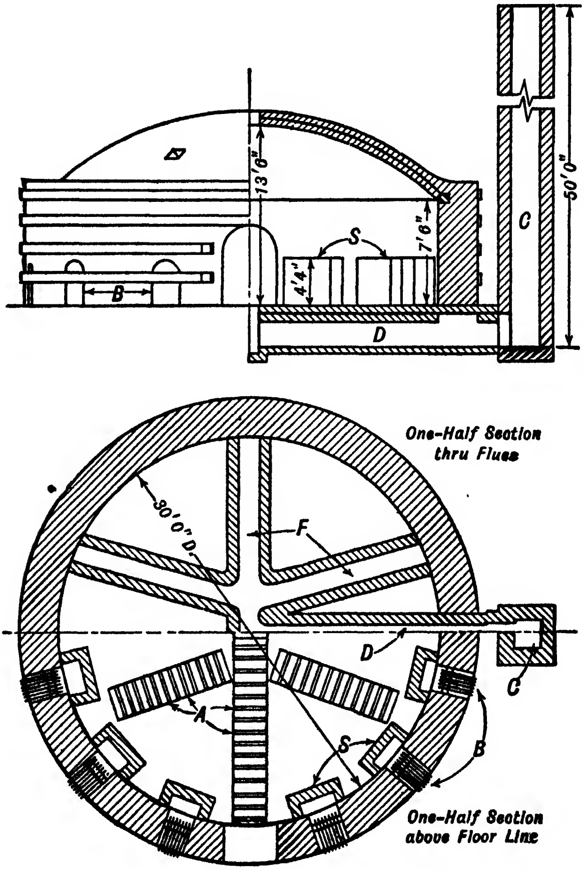

Fig. 4. A Down-draft Periodic Brick Kiln.

Up-Draft Kilns. A common type of kiln especially used in the pottery industry is the periodic up-draft kiln, shown in Figure 3. In the kiln shown, eight furnaces *B* (oil burners in this case) supply the heat. The hot products of combustion pass from the furnaces along under-floor flues *F*. Some of the hot gases in this flue pass up through short stacks or "bags" *S* and into the kiln, while others pass along the flues to the center and up through the opening *W*. The hot gases then pass up among the wares in the kiln, and up through openings in the crown and out the stack.

Down-Draft Kilns. Another common type of kiln is the down-draft periodic crown kiln shown in Figure 4. This type of kiln is commonly used for firing all types of heavy clay products, including bricks, refractories, hollow structural tiles and sewer pipes. The kiln illustrated has twelve furnaces *B*, equipped with grates for burning coal. The hot gases from the furnaces pass up the bags *S*, and up toward the closed crown. There they are deflected downward and pass among the wares and then into the under-floor flues *F*, through openings *A* in the flue covers. The gases then pass along flue *D*, and out the chimney *C*. Openings in the crown aid in the cooling of the kiln. A 30-foot kiln will hold about 100,000 face bricks.

Continuous Kilns. All periodic kilns are wasteful of fuel. This waste can be reduced to some extent by utilizing the heat from cooling kilns to dry the bricks in the driers. Continuous kilns, also known as tunnel, ring, and economizer kilns, have for their purpose still greater economy in fuel. The chamber kiln, which is a type of continuous kiln and one form of which is shown in Figure 5, was first put into practical operation in Germany in 1858 and is known as the Hoffman kiln, although it has undergone many improvements over the original design. The kilns or chambers are built in series in the form of a closed circle, flattened oval, or a rectangle, with removable partitions or with connecting flues. The cooling chambers serve to preheat the air for the chambers in fire and the hot products of combustion from the chambers in fire dry, heat and water-smoke the chambers that have been set with bricks that are getting ready for fire. The compartment that has cooled and is about ready to be unloaded is adjacent to the compartment that is being unloaded and is separated from it by a removable partition or damper of metal or paper. The loading, unloading, cooling, firing, and drying proceed from chamber to chamber progressively in a continuous cycle. Each compartment is connected by a flue to a central stack or individual stack but all are closed by dampers except one or two near the chamber that has just been set and is drying. The fuel in the form of slack coal is fed through openings in the roof, and in some cases also through openings at the sides near the bottom.

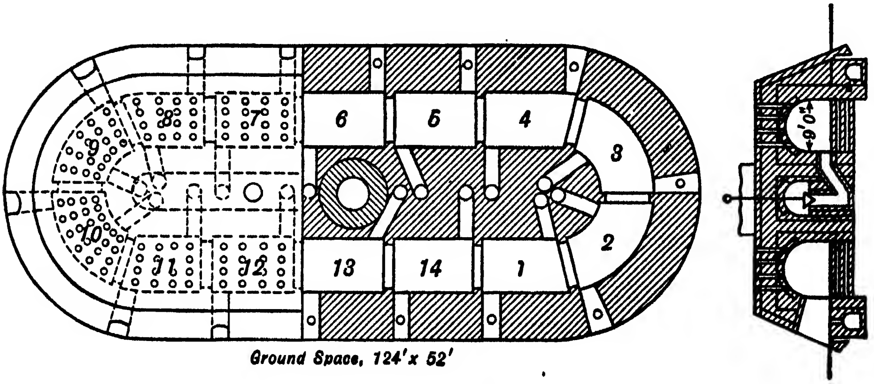

FIG. 5. A Continuous Chamber or Hoffman Kiln.

Car Tunnel Kilns. The car tunnel kiln, Figure 7, has come into prominence in recent years but its introduction antedates that of the Hoffman compartment tunnel kiln. In the car tunnel kiln the wares to be fired are placed on cars that pass slowly through a long tunnel about 130 to 500 feet long which is heated to its maximum temperature near the middle of its length. As the cars enter the comparatively cool charging end of the kiln they slowly approach the hot zone so that water-smoking, dehydration, and vitrification progress in the wares as the cars pass through the zones of corresponding temperatures. After the cars pass the burner zone they enter the cooling zone in which the temperature gradually decreases toward the discharging end so that the wares are cooled slowly. The kiln is full of cars its entire length, the cars being moved slowly by a pusher or other mechanical device. When the cars leave the tunnel they move at right angles along a short transverse track and then back to the charging end on a track parallel to the tunnel. While the cars are on the return track they are unloaded and reloaded with fresh wares to be fired. The fuel economy of a car tunnel is about equal to that of a large kiln of the Hoffman type. The hot zone of the kiln is centralized, being in a region

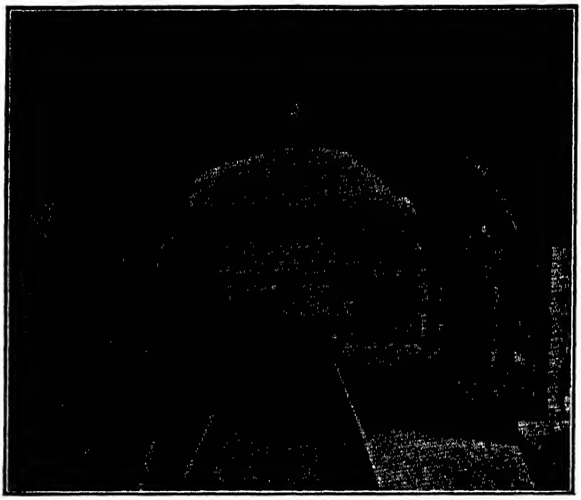

FIG. 6. Chamber Kiln Showing the Temporary Track for the Cars and the Paper Partition Back of the Setting of Bricks. This paper partition burns out as the fire advances.

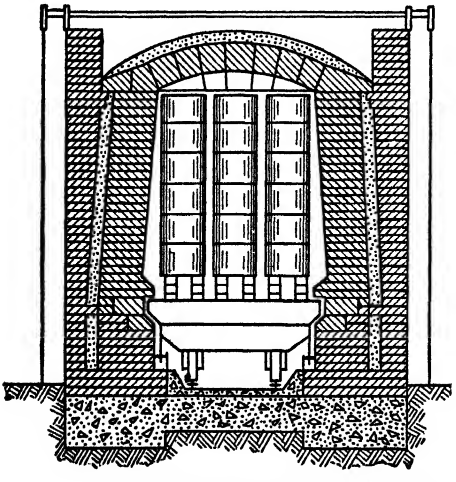

FIG. 7. A Cross-sectional View of a Car-tunnel Kiln.

about 35 to 40 feet long; only this zone requires high-grade refractories. The car tunnel kiln is used in a wide variety of plants producing practically all types of fired clay wares. A cross-section of one type of car tunnel kiln is shown in Figure 7. The car is loaded with saggers filled with white ware. The top of the car is about 4 feet wide, and the kiln will hold 40 to 60 cars.

Circular Tunnel Kiln. The circular tunnel kiln is one of the newest developments in kiln design. In some respects it is similar to a car tunnel kiln, but instead of being straight, the kiln is built in the form of a circle so that the entrance end and the discharge end of the kiln come fairly close together as shown in Figure 8. The ware, instead of being placed on individual cars, is placed on a large horizontal ring which carries a refractory clay slab on its top on which the ware is set. The ring turns slowly carrying the ware through the kiln just as cars carry ware through a straight kiln. As the ware comes out the discharge end it is removed and new ware is put in its place, the operations being performed as the ring continues to move. This type of kiln is adapted to firing nearly all types of wares from fine china to heavy clay products.

Measuring Kiln Temperatures. Various methods are in use for measuring kiln temperatures or heat conditions in the kiln. One of the oldest methods is the use of pyrometric cones, also called Seger and Orton cones. The cones are actually slender pyramids about 2 in. long; they consist of mixtures of clays and fluxes, graded to give a series of fusion points. Cone No. 021, corresponding to about 615° C., consists of

$$\left.\begin{matrix}0.5\,Na_2O\\0.5\,PbO\end{matrix}\right\}0.1\,Al_2O_3\left\{\begin{matrix}2.2\,SiO_2\\1.0\,B_2O_3\end{matrix}\right.$$

(The figures represent the approximate molecular proportions.)

The cones soften and finally melt as the temperature increases; a cone is said to be "down" or to have reached its "end point" when it has bent under its own weight so that the apex touches the base on which the cone is mounted. The end points of a few pyrometric cones for different rates of heating are given in Table 3.

TABLE 3—END POINTS OF PYROMETRIC CONES *

Cone No.	*20° C. per Hour* † *End Point*	*150° C. per Hour End Point*	*Cone No.*	*20° C. per Hour End Point*	*150° C. per Hour End Point*
020	625° C.	650° C.	1	1125° C.	1160° C.
015	770	805	5	1180	1205
010	890	895	10	1260	1305
05	1030	1040	15	1410	1435
01	1110	1145	20	1520	1530

* For a complete table see Fairchilds, C. O. and Peters, M. F., Jour. Amer. Ceram. Soc., *9*, 738 (1926); Anon., ibid., *11*, 340 (1928); Ries, H., "Clays: Their Occurrence, Properties and Uses," third edition, p. 309, John Wiley & Sons, Inc. (1927); Andrews, A. I., "Ceramic Tests and Calculations," p. 126, John Wiley & Sons, Inc. (1928).

† Refers to rate of temperature rise.

The softening point of the cones depends upon the rate of heating and the atmosphere in the kiln[13] and cannot, therefore, be used as precise temperature

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[13] See "The Function of Time in the Vitrification of Clays," Bur. Stds. Tech. Paper No. 17.

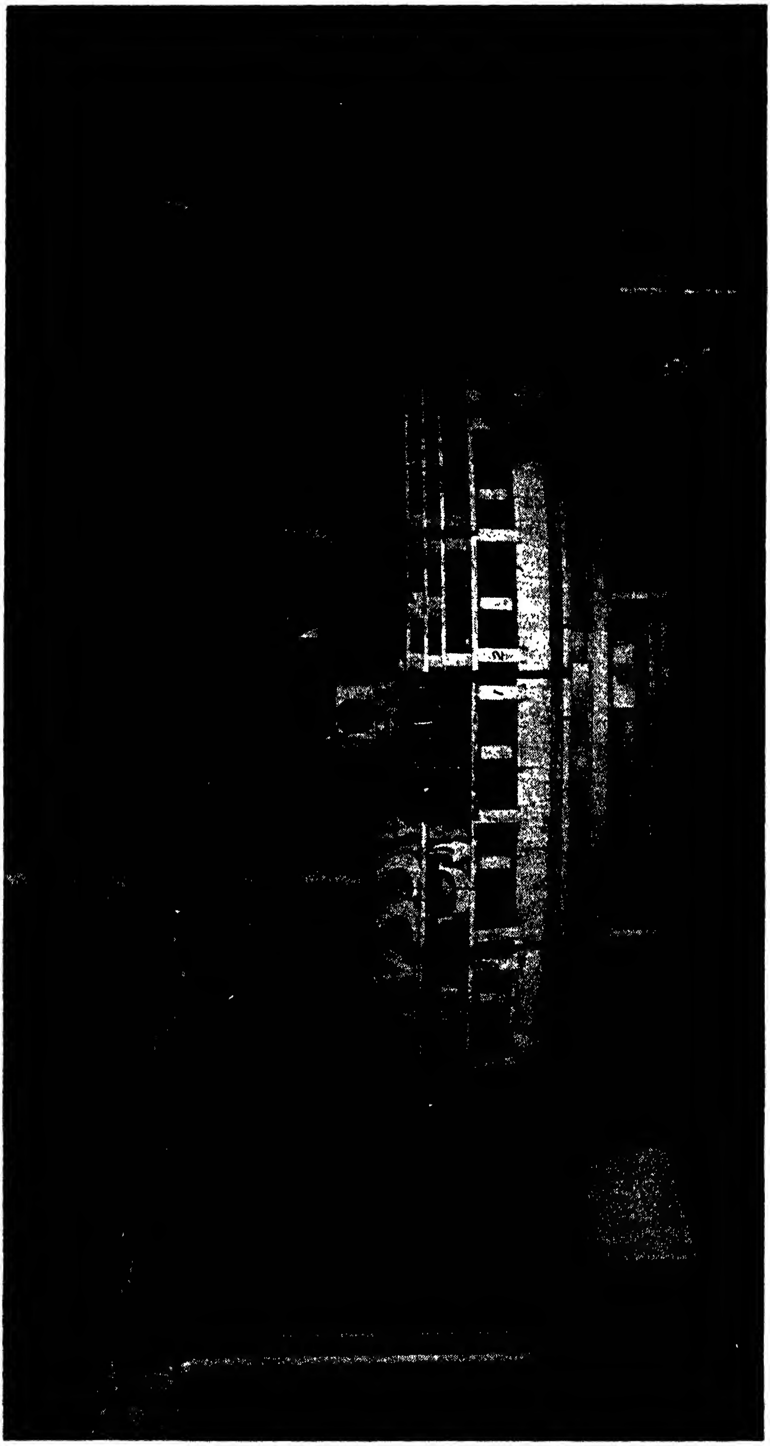

FIG. 8. A Circular Kiln.

indicators. Cones are used extensively in the pottery industry, but pyrometers now supplement them in many of the larger potteries.[14]

Veritas or firing rings are also used. They consist of clay mixtures, their contraction with heating being a function of the temperature. They, like cones, have specific usefulness in that they can be placed in saggers or other inaccessible parts of the kiln, and on account of their cheapness can be used in large numbers. Trial pieces, consisting of rings or bars made of the same material as the ware in the kiln, may also be placed in pottery kilns with the ware. From time to time a trial piece is removed to note progress of the firing. Recording thermocouples are now finding extensive application for measuring kiln temperatures and practically all users of tunnel kilns keep a graphic record of temperature conditions in different sections of the kiln. For temperatures above the range of thermocouples, optical and radiation pyrometers are used.[15]

MANUFACTURE OF HEAVY CLAY PRODUCTS

The term "heavy clay products" commonly used in the clay industries includes bricks, sewer pipe, drain tile, hollow block, terra cotta, flue linings, conduits, roofing tile and fire clay refractories. These wares are usually made from clay directly as dug except that the clay is ground, and in some cases screened, and tempered. In fire brick manufacture several clays may be mixed together.

The manufacture of all the various kinds of heavy clay products cannot be discussed here but a few types will suffice to give a general view of the processes.

Bricks—Brick-making is one of the oldest of the ceramic arts. Bricks said to have been made by the Babylonians 6000 years ago are still in good condition.

Preliminary Preparation of Clays. Relatively low grades of clay are suitable for brick manufacture. Some clays can be made into bricks directly without any preliminary treatment but others require special preparation, and therefore are subjected to one or more of the processes of weathering, grinding, pugging and tempering as previously described.

Soft-Mud Process. The soft-mud process is the oldest method of making bricks. The clay is worked up with sufficient water to make a soft mud that can be easily pressed into wooden molds, either by hand or by machines. The molds are sprinkled with sand on the inside to prevent the brick from sticking; this sand shows in the finished brick. A modern power-driven soft-mud brick machine has a capacity of from 1000 to 5000 bricks per hour. A large variety of clays are suitable for the soft-mud process, and the bricks if properly fired are of excellent quality with well-defined edges, of a solid homogeneous structure and have the property of withstanding the action of frost very well. The soft-mud process is especially used in making fire bricks.

Stiff-Mud Process. The stiff-mud process is a more modern development of the brick industry. The clay is ground and pugged just as in the soft-mud process, but the amount of water added is much less. The mud is just soft enough to be squeezed through a die under pressure, but stiff enough for the

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[14] For a further discussion of temperature measuring instruments see Chapter 5.

[15] For a review of pyrometric practice in ceramic industries see "Pyrometric Practice," Bur. Stds. Tech. Paper No. 170, and Brown, Jour. Amer. Ceram. Soc., 7, 620-5 (1924).

bricks to hold their shape in handling. The mixed and pugged clay mud is fed into an auger machine, Figure 9, in which a tapering auger forces the clay through a die. The clay comes out of the die in the form of a bar whose cross-sectional dimensions are equal to one face of the brick. The clay bar passes along a short belt conveyor onto a cutting table, Figure 10, on which a frame with a number of wires automatically cuts the bar into bricks. While the wires are passing through the clay they, with the frame, move in a direction parallel to the motion of the clay and at the same velocity. This insures a cut at right angles to the bar. After each cut the frame moves back to its original position. The stiff-mud process is very popular on account of its automatic features and large output. The clay requires no attention from the time it enters the pug mill until the cut bricks are removed from the belt conveyor. Stiff-mud machines have capacities up to 15,000 bricks per hour, which is greater than that of any other type of machine. The bricks, however, have a tendency toward a laminated structure on account of the center of the clay bar passing through the die faster than the sides where frictional resistance is greater. If the die is not lubricated properly (with steam, oil, water or by electrical means)

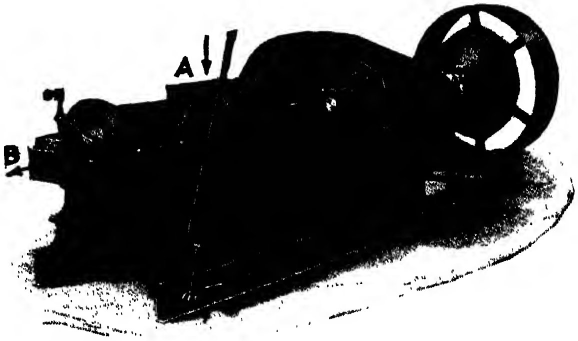

Fig. 9. Auger Machine.

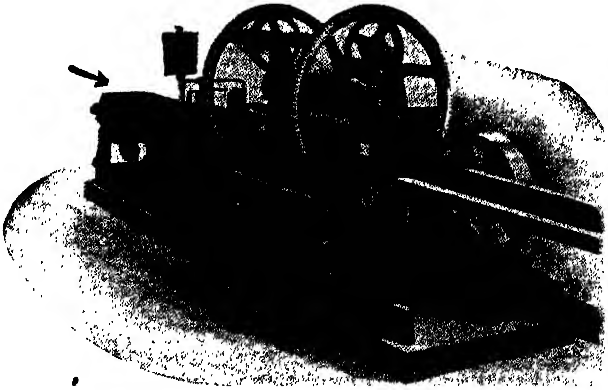

Fig. 10. Cutting Table.

the edges of the bar of clay become serrated. The stiff-mud process also requires closer regulation of the plasticity of the clay than do the other methods.[16]

If the bricks from the soft-mud and stiff-mud processes are to be used as face bricks they may be repressed in a repressing machine. Repressed bricks are compact, perfectly dimensioned with edges and corners clearly defined. Repressing is done in hand presses or in power presses, the latter having a capacity up to 3000 bricks per hour.

Dry-Press Process. In the dry-press process the dry clay containing usually less than 15 per cent moisture is fed from overhead bins into the press hopper through canvas tubes. As the machine operates, the charger moves over the mold, fills it and withdraws. Top and bottom plungers then move toward each other in the mold, subjecting the clay to very great pressure, producing a dense compact brick with well-defined and smooth faces. The bricks tend to be of a stratified texture if not carefully prepared. The clay must be thoroughly ground and pulverized and should be screened through a 16-mesh or finer screen. The bricks from the dry-press machine, Figure 11, may be set in the kiln directly, but it is considered preferable to give the bricks a preliminary drying.

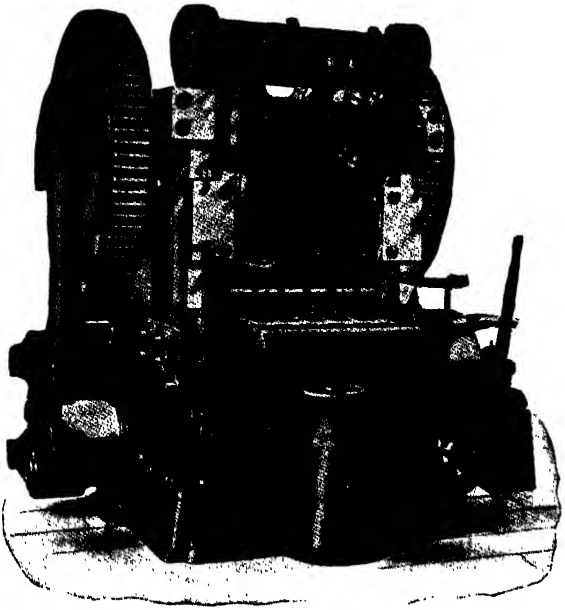

FIG. 11. Dry-press Brick Machine.

Semi-dry-pressed bricks are made in a manner similar to the dry-pressed except that the clay contains more moisture.

Efflorescence. Efflorescence, also called whitewash, drier white, kiln white, wall white, sulfation, and scumming, refers to discoloration on the surface of clay products due to soluble salts in the clay. This discoloration may take

[16] Barker, G. J., and Truog, E., Jour. Amer. Ceram. Soc., *21*, 324-29 (1938).

place in the driers (drier white) due to salts being concentrated on the surface as the water evaporates. Calcium and magnesium sulfates are the most bothersome. If the ware is exposed to sulfur dioxide fumes caused by sulfur in the fuel, calcium and magnesium carbonates in the clay may be decomposed in the presence of moisture to the corresponding sulfates. This may happen in the kiln (kiln white) or in the drier if it is heated by waste kiln gases. The calcium and magnesium sulfates thus formed may not show when the ware is removed from the kiln, but if the bricks are exposed to the weather, moisture absorbed by the bricks will concentrate the salts on the surface as it evaporates, forming wall white. Efflorescence may be overcome by working the clays before soluble salts are formed by weathering, or by letting the clay weather completely so that soluble salts are removed by leaching; by drying and firing the ware rapidly to prevent concentration of the salts on the surface; by avoiding sulfur-containing fuels; firing the ware in reducing atmosphere; or by precipitating the soluble sulfates with barium salts.

Drying. Bricks are dried outdoors, or in sheds, and more commonly in car tunnel dryers.

Firing. Bricks are commonly fired in scove kilns, periodic down-draft kilns, Figure 4, continuous kilns, Figures 5 and 6, and car tunnel kilns, Figure 7. The firing range is generally between cones 012 to 06 (875° to 1015° C., or 1787° to 1858° F.).

Production. Common brick production reached a maximum in 1923 when the value of the bricks manufactured equalled $94,500,000. The depression low in 1932 was $8,700,000 after which the increase was fairly regular. The peak production of face, fancy and enamelled bricks amounted to $47,000,000 in 1925.

The state of New York leads in the production of common bricks, producing approximately 11 per cent of the national production, Pennsylvania and Illinois following in order. Ohio leads in face brick manufacture, producing approximately 17 per cent of the total, with Pennsylvania and Illinois following in order.

Sewer Pipe Manufacture—Sewer pipes are made mainly from shale tempered with fire clay. Sewer pipes are made in special presses, Figure 12, by the stiff-mud process. The press consists of two cylinders in tandem with axis vertical. The upper is the power cylinder operated by steam; the lower is the clay cylinder from which the prepared clay mixture is extruded downward through a die at the bottom. The process is, therefore, intermittent. A counterbalanced table free to move vertically is placed below the die to receive the pipe as it is expressed. The pipe is cut into proper lengths by a power cutter or by a wire operated manually. Special shapes as elbows and traps are made by hand in plaster molds.

Some sewer-pipe presses can be fitted with a "goose neck" at the bottom of the clay cylinder. The clay is then expressed horizontally instead of vertically. The "goose neck" may be fitted with dies to make bricks or structural hollow ware.

Sewer pipes are salt glazed; the pipes are set on end in the kiln unprotected from the flames. When the kiln is up to temperature, cone 1 to 11 (1125° to 1285° C., 2057° to 2345° F.), salt is put in the fireplaces, a few shovelsful at a time, over a period of several hours. The salt volatilizes at the high temperature and combines with the clay, forming a glaze on the surface. All clays are not adapted to salt glazing. Salt glazing is also applied to some stoneware.

Sewer pipe production reached a peak in 1923, when the value of the product amounted to $32,500,000; the present production is approximately half this amount. Ohio, Pennsylvania and California are the chief producing states.

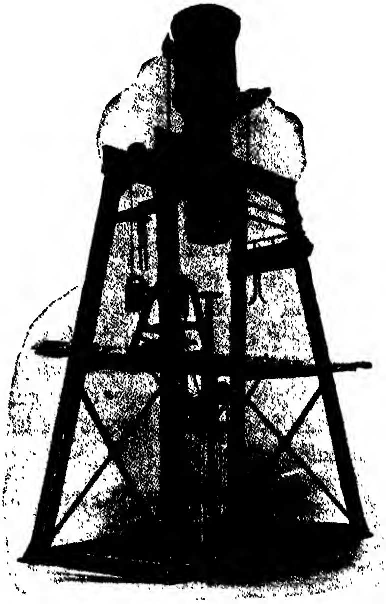

FIG. 12. A Sewer Pipe Machine.

Hollow Structural Tile—Included in this classification are fireproofing terra-cotta lumber, hollow blocks and hollow bricks, some of which are shown in Figure 13. The fireproofing materials are those which are employed in floor arches, partitions, and wall furring for girders and columns. Terra-cotta lumber is a soft and porous material produced by mixing sawdust with clay and subsequently burning it out. It is not fired very hard and can be nailed and sawed the same as lumber. Hollow blocks and hollow brick are used for outside walls.

Hollow ware is made by the stiff-mud process by auger machines. Many stiff-mud brick machines have interchangeable dies so that they can be used not only for making bricks, but also for a great variety of hollow ware. Sewer-pipe presses can also be fitted with dies for making hollow structural material.

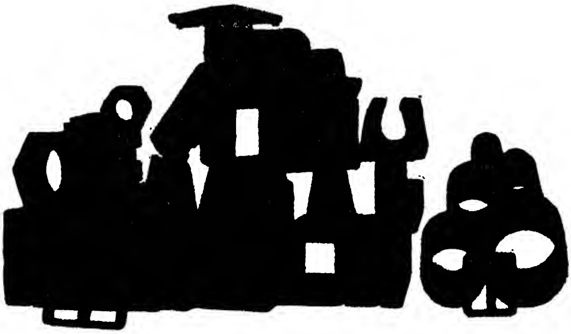

FIG. 13. Hollow Structural Tile.

The maximum annual production of hollow structural tile to date was in 1929 when the value of the product was $30,500,000. Ohio, New Jersey and Iowa are the chief producing states.

Terra Cotta—Terra cotta denotes hand-made clay products for structural decorative purposes. Semi-fire clay mixed with a low grade of clay or shale and grog (ground firebricks) is commonly used for terra cotta. The ware is formed either by hand modeling or in plaster molds and requires a great deal of skill. On account of the large bulky shapes frequently made, the drying must be carried out very carefully to prevent warping and cracking. Although most terra cotta is glazed, the body is not given a biscuit fire, but the glaze is sprayed in the form of a slip directly on the dried green ware. Terra-cotta is fired in muffle kilns at temperatures varying from cone 010 to 8 (895° to 1260° C., 1643° to 2300° F.).

Tile—Under this heading come roofing tile, floor tile, and wall tile. For roofing tile the clay is prepared similarly as for bricks although more care is used. Simple forms can be expressed from auger machines and cut into proper lengths. Other forms are made by repressing slabs of clay. Floor tiles are made from a body similar to whiteware from fire clays, buff-burning clays or shale. They are fired to a dense body at cone 8 to 12 (1260° to 1335° C., 2300° to 2435° F.). Wall tile are made in dry press machines from a white burning body but fired at a temperature considerably below that of vitrification. The shapes are first given a biscuit fire in saggers and are then glazed and glost fired in a muffle kiln.

FIRE CLAY REFRACTORIES

Fire clay refractories are among the earliest manufactured refractory materials, and at the present time, on the basis of tonnage, represent more than all other types of refractories manufactured.

Fire clays, the properties of which are described earlier in the chapter, are widely distributed. Pennsylvania is the chief producing state followed closely by Missouri and Ohio.

Methods of Manufacture—Fire clay refractory shapes are manufactured by the various methods used for making building bricks, including the dry press, stiff-mud, soft-mud and hand-made processes and some shapes are made by casting the thin clay slip in plaster of paris molds. Massive shapes must be dried very carefully to prevent cracking and warping. The dried shapes are fired in various types of kilns such as down-draft, car tunnel and circular kilns.

Characteristics of Fire Clay Refractories—Certain properties are desirable in refractories and these will vary according to the uses to which the refractories are put. For instance, for a boiler setting or a kiln lining, low heat conductivity is usually desired, while for use in muffle, high heat conductivity is desired.

Resistance to High Temperatures. As a rule a fire clay refractory should be able to resist temperatures of at least 1600° C. (2912° F.), without softening and some of the high alumina clays may be put to use in furnaces in which they will encounter temperatures above 1800° C. (3272° F.). The temperature at which a refractory can be used satisfactorily depends to a large measure upon such factors as load, chemical nature of the charge or slag, oxidizing or reducing conditions and the abrasion to which it is subjected. Fire clays that soften between 1500° C. (2732° F.) and 1600° C. (2912° F.) are sometimes classed as semi-fire clays or low heat duty clays.

Load-Bearing Capacity. Refractory linings of furnaces are ordinarily not expected to carry the load of the superstructure of the furnace, such as the boiler in boiler furnaces. This load is carried by common bricks encasing the refractory structure and therefore not subjected to any high temperatures. The refractories usually carry only the load of the other refractory materials resting on them. Fire clay refractories have a tendency to shrink under load at high temperatures, the degree of shrinkage permitted again varying with the nature of the service. In a standard test[17] the refractory is heated under a load of 25 lb. per sq. in. A high heat duty brick should not deform a great deal at 1350° C. (2462° F.), an intermediate heat duty brick at 1300° C. (2372° F.) and a moderate heat duty at 1100° C. (2012° F.). In the earlier specifications the actual deformation permitted for each class was specified, but at present this is not as rigid, except that a high heat duty brick containing 70 per cent or more of silica should not shrink more than 4 per cent or expand more than one per cent at 1350° C. (2462° F.) under the above conditions.

Spalling. When bricks are subjected to a temperature gradient there will be uneven expansion or contraction with the result that a stress is set up between different parts of the brick or other refractory ware, which may be of sufficient magnitude to cause pieces of the brick to break off. This breaking off, called spalling, may also be caused by compression in the structure due to expansion of the whole from a rise of temperature, or may be due to slag penetration into the brick, thereby causing variations in the coefficient of expansion. Spalling may be reduced by avoiding sudden temperature changes, or by modifying the furnace design so stresses are not set up as the furnace heats. If the spalling is the result of uneven expansion due to slag penetration into the brick, the spalling can be reduced by originally firing the bricks at a temperature greater than their operating temperature. This reduces the pores in the brick and checks slag penetration. However, such a brick is dense and rigid and cannot adjust itself to relieve strains caused by uneven heating. If contact of slag with the brick is avoidable, spalling caused by thermal shock can be reduced by making a relatively porous brick. Such a brick can more readily expand unevenly without spalling.

Chemical Properties. Refractory materials may come in contact with slags or other materials in the furnace that will react with the refractory and thereby reduce its useful life. Since it may be impossible to eliminate chemical action between the refractory and the charge, efforts may be successful in reducing the rate of reaction and thereby prolong the life of the refractory. Some of the chief methods for reducing the rate of reaction are the following. 1. Since chemical reactions increase in velocity with rise in temperature a logical attack would be to operate the furnace at lower temperatures. However, most furnace processes require a certain temperature and this method of attack is not practical. It is possible to cool the furnace walls from the outside and thereby reduce the interfacial temperature between the charge and the refractory. This necessitates considerable heat loss but is common practice in glass tanks. After the tank wall has become thin due to the reaction between the glass and the tank blocks, air blasts or water coolers are used to cool the refractory and thus extend

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[17] A. S. T. M. Designation C 16-20.

its life. 2. If the refractory is of the same chemical nature as the charge or slag, reaction will be slow. For this reason it is generally recommended that acid refractories be used with an acid charge and basic refractories with a basic charge. At moderate temperatures, however, chemical action may be so slow that the refractory and charge may be of opposite chemical nature, as is the case in a lime kiln lined with silica refractories. In these cases other factors such as abrasive resistance become more important than those of chemical nature. Fire clay refractories are acidic in their nature, unless they contain much excess alumina, in which case they may be basic. 3. The rate of reaction depends also upon the surface exposed. If a refractory is porous, slag can penetrate the pores and on account of the large surface for attack reaction may be rapid. A dense brick thus resists corrosive reaction much more readily. 4. If the slag or charge flows rapidly over the brick surface, the reacted material is washed away and fresh surface is exposed for more attack. Thus, a fluid slag that flows down a refractory wall rapidly will wear down the wall much faster than a viscous slag that accumulates and moves slowly.

Heat Transmission. Heat may be transmitted through refractories by conduction and by radiation.[18] Convection is of little importance in transmitting heat through furnace walls, but may be of great importance in carrying the heat from the interior of the furnace to the walls. In a dense refractory the heat is carried through the walls by conduction. If the refractory is porous, convection of the gases in the tiny pores is relatively unimportant in aiding heat transmission, but at higher temperatures radiation across the pores becomes important. Since the amount of heat radiation is proportional to the difference between the fourth power of the temperatures, radiation becomes of increasingly more importance with rise in temperature. The more porous a refractory, the greater is its resistance to heat transmission, especially at low and moderate temperatures. At high temperatures radiation across the pores becomes more important and the insulating qualities are reduced. As a rule, it is desirable to have a furnace lined with refractories of low heat conductivity to reduce heat loss, but in some cases this causes the inner surface of the refractory wall to reach such high temperatures that its life will be reduced. Therefore it is desirable in some cases to use walls having good heat conductivity and to cool the walls from the outside. For muffles, in muffle furnaces where the charge and the flame are separated by a refractory wall, a refractory possessing good heat conductivity is desirable.

Use of Grog in Refractories—As a rule, fire bricks are not made from a single raw clay, for the firing shrinkage would be high and the porosity of the brick would be low. A high firing-shrinkage causes cracking and warping of the refractory and it is difficult to produce the finished product to close dimensions so desirable in refractories. Most refractories are made from a plastic clay and a grog. The grog is a granular, non-plastic material consisting of flint fire clay or of fire clay that has been fired in a kiln and then ground to a granular form. Broken, cracked and warped fire bricks are commonly ground to make grog, but grog is also produced by firing clay especially for this purpose.

Increasing the amount of grog in a refractory up to about 70 per cent con-

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[18] For a discussion of the principles of heat transfer see Chapter 2.

tinually reduces the firing shrinkage. After this point the addition of grog has little effect on the shrinkage. The size and amount of grog affects the spalling characteristics of the brick.[19] In the range from 2 to 20 mesh the spalling resistance increases with increase in the *size* of the grog particles. An increase in the *amount* of grog up to approximately 50 per cent increases the spalling resistance of the bricks.

Insulating Refractories—The use of insulating bricks for backing-up refractories to conserve heat has been common practice in many installations. A number of refractory manufacturers are now making a porous refractory brick that has heat insulating properties itself. Among the advantages of using such insulating refractories may be mentioned [20] saving in heat storage, reduced time in bringing the furnace to temperature (for a given rate of firing a furnace lined with insulating refractories may be brought up to temperature in from 25 to 35 per cent of the time for a furnace with a firebrick lining), and saving in fuel, the saving amounting to 20 per cent and over for a fully insulated furnace.

The heat insulation is obtained by producing a porous brick. Insulating refractories have a bulk density ranging commonly between 45 to 50 lb. per cu. ft., as compared to 120 to 140 lb. per cu. ft. for firebricks. The porosity may be obtained by,[21] 1. adding a combustible material such as coal or sawdust to the refractory mix, which burns out in the kiln, 2. aerating a powdered body, 3. bloating the mix in slip [22] form by gas evolved by chemical reaction, or 4. developing a stabilized foam in a refractory mix in slip form.

Shapes of Fire Clay Refractories—The refractory manufacturer may be called upon to supply over 3000 different fire clay sizes and shapes. Of these over a hundred are in such common use that they are called standard shapes. The most common size is what is usually called a firebrick, technically known as a standard 9-inch straight, measuring 9 in. by 4½ in. by 2½ in. A unit half as thick is called a split, one half as wide is called a soap. Other standard shapes are wedges, keys, skews, cupola blocks, checkers, tiles, baffles, and flue liners.

Refractory Mortars and Cements—Firebrick are customarily laid up with a mortar in slip form consisting of ground fire clay and water. The mortar is applied with a brush, or the face of the brick may be dipped into the slip. Only enough mortar is used to fill up any irregularities in the surface of the bricks, for the bricks must actually rest on one another.

Cements in plastic form are also used for patching walls and for constructing walls. Such cements may contain a number of ingredients, raw clay and grog being in wide use. For some cements sodium silicate is added. This makes the cement air setting to hold it in place until the first firing. Plastic refractories are used widely for building up refractory walls especially in boiler furnaces, generally referred to as monolithic walls.

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[19] Norton, F. H., "Refractories," p. 362, McGraw-Hill Book Co., Inc., New York (1931).

[20] Hepburn, W. M., Jour. Amer. Ceram. Soc., *18*, 13-17 (1935).

[21] Rueckel, W. C., Jour. Amer. Ceram. Soc., *18*, 18-22, especially 18 (1935); Foster, H. D., Bull. Amer. Ceram. Soc., *19*, 468-473 (1940).

[22] A "slip" in ceramics refers to a mix of ceramic material such as clay with sufficient amount of water to make it pour easily. Desired fluidity can be obtained with much less water if about 0.5 per cent alkali is added.

A refractory cement called "Lumnite," consisting essentially of calcium aluminate, has many of the properties of a Portland cement (calcium silicate) and in addition is refractory. It can be mixed with a refractory aggregate such as old firebricks or a variety of other materials ground to proper size to make a refractory concrete that can be placed in the same manner as ordinary concrete, and has similar air setting properties.

CHEMICAL STONEWARE

Chemical stoneware is used widely in industry to resist acid solutions and also mildly alkaline solutions. It is used for pipes, stop-cocks, acid pumps, montejus, chlorinating vessels, condensers, retorts, stills, packing for absorption and scrubbing towers, pickling baskets, and a variety of other purposes. The physical properties of chemical stoneware are summarized in Table 4.[23]

TABLE 4—PHYSICAL PROPERTIES OF CHEMICAL STONEWARE

Ultimate compressive strength, lb. per in.^{2}	82,000-115,000
Ultimate tensile strength, lb. per in.^{2}	1,650- 4,300
Modulus of elasticity, lb. per in.^{2}	$1.05\text{-}5.95 \times 10^6$
Specific heat	0.2
Thermal conductivity, B.t.u. per ft.^{3}	0.78-2.05
Linear expansion, per ° F.	$1.9\text{-}2.3 \times 10^{-8}$
Ultimate bending strength, lb. per in.^{2}	5,900- 12,500

The chemical composition of stoneware is usually between the following limits: SiO_2 60-70 per cent, Al_2O_3 20-25 per cent, Fe_2O_3 0.8-1.8 per cent, $CaO + MgO$ 0.5-1.2 per cent, $K_2O + Na_2O$ 1.5-3.5 per cent. The best grades of stoneware are considered to contain approximately 70 per cent SiO_2 and 22-23 per cent Al_2O_3. Chemical stoneware is closely related in its composition and properties to porcelain. In fact, for small articles, especially for laboratory use, porcelain is used, and it can be considered a high grade, highly refined chemical stoneware.

Clay for chemical stoneware is carefully selected, and it is usually necessary to blend two or more clays to produce the desired properties. The clay should contain little iron oxide and lime compounds, and $CaCO_3$ especially should be absent. The clay should vitrify at about cone 9 (1250° C. or 2282° F.) and should produce a dense texture. Grog in the form of ground stoneware is necessary for the manufacture of all but smallest pieces of ware. The grog is ground so that all will pass through a 60-mesh screen, but a good share should be retained on a 200-mesh screen. For some clays it is necessary to add 5 to 10 per cent feldspar as a flux in order to produce a dense body.

The raw materials are crushed and screened and then mixed with excess water in a blunger. On leaving the blunger the slip is passed through a magnetic separator to remove the iron-bearing particles. The slip is then filtered in a press to remove excess water and some of the objectionable soluble salts. The plastic filter cakes, the grog, and any feldspar are thoroughly pugged in a pug mill. The pugged body is then stored in cool moist vaults for two weeks to improve the plasticity.

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[23] Chem. & Met. Eng., *39*, 651 (1932).

The plastic material is formed into desirable shapes by one of several operations, such as jiggering, extruding, hand pressing, casting, and dry pressing.

The ware is carefully dried and can be fired in any of the types of kilns used for firing heavy clay products, the down-draft kiln being generally used for this purpose.[24] It is salt-glazed in the kiln, but the inside of the ware may receive a special glaze for better chemical resistance.

Chemical stoneware is not a good heat conductor and cannot withstand severe thermal shock. To obtain sufficient mechanical strength the walls are made relatively thick which further hinders heat transfer. Thus for heating or cooling solutions in stoneware the heat is seldom transferred through the container wall. Cooling or heating coils are placed inside the container. These coils may be made of chemical stoneware, for the wall sections of pipes can be made relatively thin.

POTTERY

Classification—The term "pottery" includes a variety of ware made of clays alone or clays compounded with other materials. Pottery may be divided broadly into earthenware and china (including porcelain) ware. A more complete classification is as follows: [25]

A. Natural body.
  1. Common earthenware, or crockery, covered with lead glazes or soft tin enamels.
  2. Stoneware.
    (a) Salt glazed.
    (b) Lead glazed.
      1. Yellow ware.
      2. Rockingham ware.
      3. Jet ware.
      4. Samian ware.

B. Compounded body.
  1. Porous, nonvitreous body.
    (a) C.C. (cream colored) ware.
    (b) Whiteware.
    (c) Ivory ware.
  2. Dense, vitreous, and translucent body.
    (a) Feldspar porcelain, high biscuit and low glost fire.
    (b) Feldspar porcelain, low biscuit and high glost fire.
    (c) Bone china, high biscuit and low glost fire.

Whiteware—A detailed description of the method of manufacture of all the above classes of pottery cannot be given here. Only that of earthenware, also called semivitreous dinnerware, will be described. It is a type of tableware possessing a white comparatively porous body, covered with a brilliant trans-

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[24] For a flow-sheet of the manufacturing process see Chem. & Met. Eng., *47*, 637-640 (1940).

[25] Ries, H., "Clays: Their Occurrence, Properties and Uses," third edition, p. 134, John Wiley & Sons, Inc. (1927). This reference also defines all the terms used.

parent glaze. Ivory ware is similar, except that the body materials have been so selected as to give a pleasing ivory tint.

Body Mixture: Composition and Preparation. A typical body composition for semivitreous tableware is given below:

	Per Cent
English china clay	14.0
Ball clay	16.0
Florida clay	6.5
North Carolina clay	14.0
Feldspar	13.5
Flint	36.0

The kaolin serves as the main body material and gives the white color to the ware. It has in itself insufficient plasticity to permit proper working on the potter's wheel. The Florida and North Carolina clays are used to replace part or all of the more expensive English clay. In the past few years much improvement has been made in the refining of domestic clays. In some ivory bodies, no English china clay is used. The ball clay is added to give plasticity and bonding power to the body. It has a tendency to give a creamy color to the fired ware and is, therefore, added to the body in the smallest amount possible. The flint adds porosity to the ware, reduces drying and fire shrinkage and resists the deformation during firing caused by the softening of the other materials. The feldspar acts as a flux; it melts to a glass at the high kiln temperatures and dissolves some of the clay and quartz and cements the undissolved particles into a firm unit. There is insufficient fusion to cause all the porosity to disappear; the porosity of well-burned, unglazed, white ware is about 8 per cent. A small amount of cobalt oxide is used to overcome any creamy color in the fired wares, unless an ivory color is desired.

The raw materials are ground up finely, mixed with sufficient water to form a slip, and then agitated in stirring machines called blungers. A blunger consists of a large tank with a revolving gate as the stirring device. It mixes the components of the body and breaks up all the agglomerated particles so that the whole mass is brought into suspension. The blunged body is passed beneath strong electromagnets to remove any particles of metallic iron and then through a fine screen or lawn. The excess water is removed from the slip by means of a filter press. The press-cakes are placed in a pug mill and are thoroughly pugged and then expressed in the form of a circular column through a die, so that pieces of desired size can be cut off with a wire. The pugged body is sometimes stored in clay cellars to increase the plasticity of the mass.

Shaping the Ware—Whiteware may be shaped by four methods, all of which are in use in American potteries.

Throwing. The thrower's wheel, Figure 14, consists of a disc fastened to the top of a vertical spindle. The spindle was originally rotated by the thrower's foot, but mechanical power is more common now. The thrower places or throws a wad of clay on the disc, and as it rotates he shapes the ware with his fingers. Throwing is the oldest method of forming pottery and is still in extensive use in Europe. In America it is used in the smaller potteries and to some extent in the larger ones for special shapes or odd pieces.

Jiggering. The process of jiggering is used extensively for making tableware. A horizontally rotating plaster mold having the shape of either the inside of flat ware (plates, saucers) or the outside of deep ware (cups, bowls) receives the clay, Figure 15. A lever with a profile shaped to conform to the outside (or inside) of the ware is lowered over the mold with its clay to a definite position so that all excess clay is removed. The mold with the formed ware is then placed in the drying room.

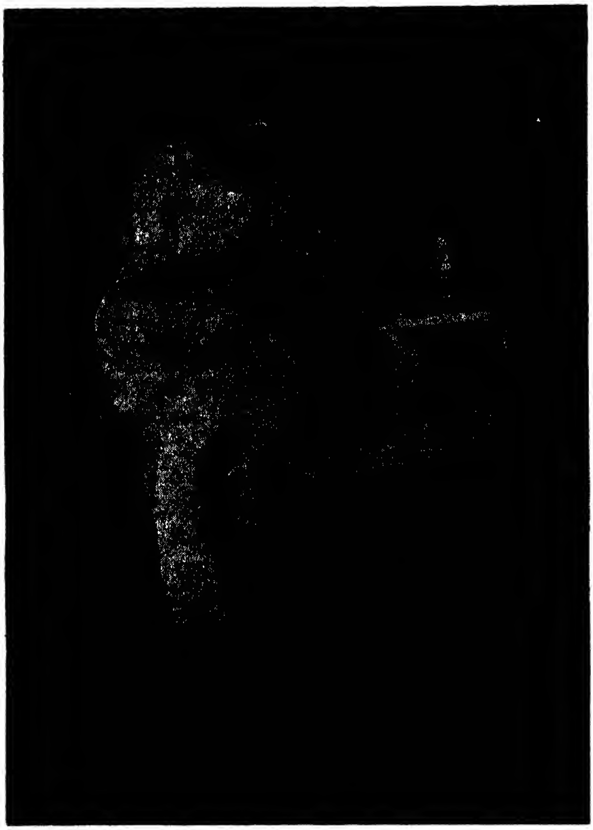

FIG. 14. A Potter's Wheel.

Pressing. Pressing is used for making vessels of oval cross-section, pitchers, and jugs. The plaster mold is made in several sections, usually so that the inside of the mold conforms to the outside of the finished clay article. Slabs of clay are pressed over the mold parts and trimmed to the proper size. The mold pieces with the clay are put together and the seams are cemented and smoothed with the aid of a wet sponge. After drying, the mold parts are removed, leaving the formed vessel.

Casting. In the casting process, a clay slip is poured into a plaster mold, the mold having the form of the outside of the ware. Some of the moisture of the slip near the mold is absorbed by the plaster, and after sufficient absorption has taken place, the excess slip is poured out, leaving a thin uniform coating in the mold. The mold is set to dry; the clay shrinks from the mold and the two can be easily separated. The plaster mold may be made of several parts to permit removal from complicated shapes. Handles, spouts, and the like may be made separately and then cemented to the vessel by means of a clay slip. In order to obtain a slip of the greatest fluidity with the least amount of water, small amounts of sodium silicate or carbonate or both are added to the slip; an easily pouring slip may contain no more than 30 per cent water.

Turning. Ware made by throwing and jiggering is sometimes finished on a lathe. The lathe has a horizontally rotating spindle like a wood-turner's lathe, to the chuck of which the partially shaped ware is attached. The ware is then finished with the aid of special tools or merely smoothed with a wet sponge.

Fig. 15. Jigger.

Biscuit Firing—The dried clay ware is first fired in a biscuit kiln in which the body is fired to the proper degree of vitrification. The ware is set in clay receptacles called saggers, which are then set in straight bungs in the kiln. The saggers serve to keep the ware in the bottom of the kiln from carrying the load of the ware above it and to keep the flames from coming in direct contact with the ware. The sagger joints are sealed with wads of clay. An up-draft crown kiln will hold from 2000 to 3000 saggers. When the kiln is loaded the door is sealed, and a slow fire is started. Ordinary whiteware requires from 40 to 50 hours for the water-smoking, oxidation, and vitrification, and 48 hours additional for cooling. The biscuit ware is fired to cones 8 to 10 (1260° to 1305° C.).

Glazing—The biscuit is glazed to prevent the porous body from absorbing moisture, and to give a lustrous appearance to the body as well as to make it easily cleanable. A glaze is a colorless glass specially prepared to have a coefficient of expansion corresponding to that of the body. The chemical composition of glazes is divided into three groups: the bases (R_2O and RO), the sesquioxides (R_2O_3) and the acids (RO_2). A glaze may have the following composition expressed in mols, more commonly called equivalents by ceramists:

$$\left.\begin{array}{l}0.20\ Na_2O\\0.05\ K_2O\\0.25\ PbO\\0.50\ CaO\end{array}\right| \left.\begin{array}{l}0.28\ Al_2O_3\\0.38\ B_2O_3\end{array}\right\} 2.86\ SiO_2$$

Borax and boric acid (which supply the B_2O_3) on account of their solubility in water must first be made insoluble by fusing or fritting with some of the other ingredients of the glaze. The recipe for a glaze for semivitreous ware is given in Table 5.

TABLE 5—RECIPE FOR GLAZE FOR SEMIVITREOUS WARE

FRIT	Parts
Borax	20
Boric acid	130
Flint	150

GLAZE	Parts
Frit	200
Feldspar	300
Clay	40
White lead	160
Whiting	110
Zinc oxide	30

The frit is ground with the other ingredients in water in a ball mill to form a slip. The cleaned biscuit ware is dipped in the glaze slip as shown in Figure 16 and then placed on shelves to dry. In some potteries a mangle is used for drying; it consists of shelves moved by chain conveyors through a heated chamber, part of the conveyor being shown in Figure 16.

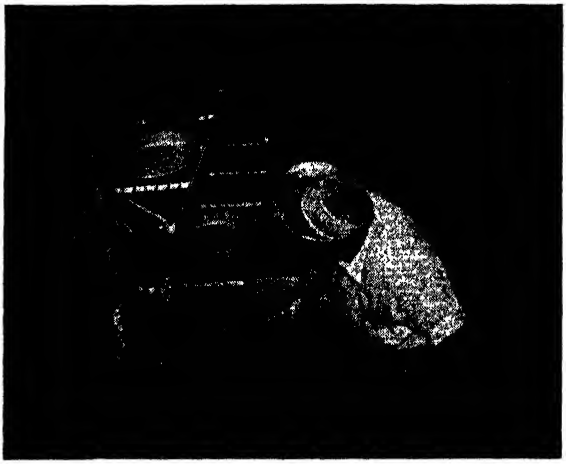

FIG. 16. Applying a Coating of Glaze to Plates by Dipping Article into the Glaze Suspension.

Glost Firing—After the glaze has dried the ware is ready for the second or glost firing. The ware is again placed in saggers but the pieces must not come in contact with one another, for the glaze on softening would cause the pieces to stick together. The pieces of ware are separated by specially shaped clay pieces called pins, which make only point contact with the ware. In order to reduce volatilization of the glaze on the ware, the saggers are coated on the inside with glaze. The firing requires from 24 to 36 hours, the temperature varying from cones 4 to 7 (1190° to 1250° C.) according to the glaze composition. The biscuit and glost firing are both carried out in periodic kilns, car tunnel kilns or in circular kilns.

A number of potteries are now producing "one-fire" ware. The glaze is applied to the unfired ware and the body and glaze are fired in one process. This not only saves the use of special kilns, and the fuel for a separate firing, but also a great deal of handling necessary for each firing process.

Decorations—Decorations are either underglaze or overglaze. Overglaze decorations permit a wider range of colors, for they need not be heated to as high a temperature as the underglaze colors, which are subjected to the heat of the glost firing (1190° to 1250° C., 2174° to 2282° F.); overglaze decorations are fired to about 750° C. (1382° F.). The coloring material is usually a metallic oxide combined with a flux. The most popular method of applying decorations is by means of transferring designs printed on special paper. Sometimes the transfer supplies only the outline of the design, which is then filled in by hand painting. Bands and lines are applied by holding brushes with the coloring material to the ware on a rotating table (decorator's whirler). Decorations are fired in a muffle kiln without the use of saggers.

PORCELAIN

If the fluxing materials in whiteware body be increased at the expense of the clay and the ware fired at a higher temperature, nearly complete vitrification will take place so that the fired body is of a translucent, glassy structure with practically no porosity. Such a body is called porcelain or china. The difference in the composition of semivitreous ware (the popular table earthenware) and china is indicated in Table 6, although the body of neither has a fixed composition.

TABLE 6—COMPARISON OF COMPOSITION OF CHINA AND EARTHENWARE

	China *Per Cent*	*Earthenware* *Per Cent*
English china clay	19.0	14.0
Florida clay	10.0	6.5
North Carolina clay	...	14.0
Ball clay	17.5	16.0
Feldspar	15.0	13.5
Flint	36.0	36.0
Dolomite	2.5	...
Average porosity of fired ware	0.5	8

If the main fluxing agent is feldspar, as illustrated in the table above, the porcelain is called spar china, if it is bone ash (calcium phosphate) it is called bone china.

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CHAPTER 22

CEMENT, LIME, AND PLASTER

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The problem of building materials is to get one that will stand the test of time. Materials which are completely oxidized are chemically stable in our atmosphere as far as oxygen is concerned and hence, are susceptible to a very long life. The supply of raw materials for producing this type of product is almost limitless, being found in the earth's crust as minerals, and most of them can be obtained at a very low cost. Hence, it would seem that such materials would be permanent and probably be a most important item in construction.

HISTORY

Man has always looked for some material to fasten other materials together. The first material to be used was clay which had been worked with water. In a general way, cement, lime and plaster can all be classed as mortars, for they are used as binders in various kinds of composite building materials. Next to iron and steel, lime and cement are now the most important building materials in use today. Various forms of lime and cement have been used for many years but they have been greatly improved during this century. As far back as the Romans, it was known that various minerals, when treated, could be used as mortar. This was the beginning of the cement industry.

The fundamental principle of making lime, cement and plaster is to take some natural materials and treat them with heat and grinding. The heat will drive off the water or carbon dioxide. When the product formed is ground and treated with water, a chemical action takes place which with the aid of air causes a reverse action to that of heating and a tendency for the product to return to its original state. The Egyptians were one of the first people to use this in the production of plaster from gypsum. Later the Greeks used the process with limestone and marble. The Romans were the first to make a cement similar to our Portland cement. The year 1756 is considered the starting point of our modern cement industry and John Smeaton, an English engineer, is given the credit.

Portland cement takes its name from the fact that it resembles in color a stone that comes from Portland, England. Joseph Aspdin, an English bricklayer, in 1824 patented a hydraulic lime which he named Portland cement from its color. Portland cement manufacture in the United States dates from 1872. Today lime and cement manufacture has become one of the principal chemical engineering industries. Chemistry has played a big part in the development of better products, especially through the use of phase rule diagrams. Engineering in the development of kilns and grinding apparatus has also improved the manufacture of cement and lime.

Economic Growth—From an economic standpoint, lime, cement and plaster form one of the most important industries in the United States. The production of these products has shown a marked increase over a long period of years, and, as a long-time trend, is still increasing as new uses are being found. Cement in many cases has taken the place of wood, iron or steel and brick. Development of plaster board and wall board has made some inroads into the direct use of lime and cement, but many of these products use either lime or cement as a binder.

Cement production in the United States increased from two million barrels in 1888 to 176 million barrels in 1928. The latter part of the 1920 decade was a period of very extensive highway and building construction. The economic depression beginning in 1929 brought a decrease in these activities and brought a serious decline to the cement industry. It slowly recovered and 1939 found the United States production back up to 125 million barrels.

CLASSIFICATION OF THE PRODUCTS

Materials which are used in various mortars may be classified in several ways but for this discussion their properties, manufacture and raw materials will be used.

1. Natural cements are made by calcining impure limestones, containing CaO, SiO_2, Al_2O_3, and Fe_2O_3, at a low temperature which will not cause vitrification. These cements do not slake, and to make hydraulic cement they must be ground.

2. Portland cements are made by calcining to vitrification an intimate mixture of calcareous and argillaceous minerals, $CaO + Al_2O_3 + SiO_2$. The resulting product does not slake when water is added. When the cement is ground after cooling it forms a cement which will hydrate to form a hard mass in the presence of water.

3. Puzzolan cements are produced by the intimate grinding of a mixture of slaked lime with slag, volcanic ash or Portland cement clinker and treated slag.

4. Common limes are made by calcining limestone, pure $CaCO_3$, forming CaO. The lime slakes with water but has no hydraulic properties.

5. Hydraulic limes are made by calcining impure limestone, containing silica, alumina and iron, at a low temperature. The resulting product will slake with water and has hydraulic properties.

6. Finishing limes are made by calcining dolomite, high magnesium limestone, at a white heat. The resulting product will slake and has special properties of whiteness and ease of working under the trowel.

7. Plasters are made by heating gypsum ($CaSO_42H_2O$) until three-fourths to all of the combined water is lost and then grinding the resulting product.

Typical analyses of the raw materials and methods of treating are shown in Tables 1 and 2.

TABLE 1—DIAGRAM OF LIMES AND CEMENTS

Raw Materials	*Heat Treatment*	*Mechanical Treatment*	*Properties*	*Classification*
Made from relatively pure limestones.	Burned at low temperatures. 600°–900° C.	Slake on addition of water to burned product.	Not hydraulic.	1. Common limes.
Made from dolomite.	White heat.			Finishing lime.
Made from argillaceous or impure limestone.	600°–900° C.			2. Hydraulic limes.
				3. Natural Roman or Rosendale cement.
Made from an intimate mixture of argillaceous and calcareous substances in proper proportions.	Burned at high temperatures. 1400–1600° C.	Do not slake on addition of water, but must be ground finely for use.	Hydraulic.	4. Portland cement.
Made from mixtures of slaked lime or Portland cement and blast-furnace slag or volcanic ash.	Not burned.			5. Slag or puzzolan cements.
Made from gypsum.	Burned at from 165°–200° C.		Not hydraulic.	6. Plasters.
	Burned at above 200° C.			7. Keene's cement, flooring, plaster, etc.

TABLE 2—ANALYSIS OF MORTAR MATERIALS *

Material	*From*	SiO_3	Fe_2O_4	Al_2O_3	CaO	MgO	SO_3	CO_2	H_2O
Lime	Glencoe, Mo.	0.15	0.85		98.01	0.45	....	0.55	....
Lime	York, Pa.	0.52	0.24		97.14	1.28	....	0.96	....
Lime	McNeil, Tex.	0.25	0.15		97.46	0.73	....	1.41	....
Lime	Tiffin, Ohio	1.61	0.17		57.44	40.36	....	0.41	....
Hydrated lime	Union Bridge, Md.	0.38	0.08	0.06	72.59	0.74	....	2.10	23.11
Hydrated lime	Carey, Ohio	0.34	0.18		45.37	31.20	....	3.02	20.07
Hydraulic lime	La Forge Cement	31.10	2.15	4.43	58.38	1.09	0.60	1.28	....
Hydraulic lime	Tiel, France	19.05	0.55	1.60	65.10	0.65	0.30	....	12.45
Plaster of Paris	Nova Scotia	0.11	0.01	0.03	38.90	0.14	54.81	0.54	5.33
Plaster of Paris	Buffalo, N. Y.	2.48	0.32	0.40	37.81	0.39	53.12	0.61	4.98
Natural cement	Cumberland, Md.	29.92	4.78	11.23	36.50	11.93	....	5.42	....
Natural cement	Rosendale, N. Y.	27.75	4.28	5.50	35.61	21.18	0.50	4.05	....

* From Meade's "Portland Cement."

Natural Cement—Natural cement was at one time manufactured extensively in this country. But owing to the cheapness with which Portland cement can be manufactured, it has been largely replaced by this latter. Natural cements are produced by burning, calcining and subsequently grinding clayey or argillaceous limestones, which are natural mixtures of calcium carbonate and clay. These limestones usually carry from 13 to 35 per cent clayey matter ($SiO_2 + Al_2 + Fe_2O_3$), and often a considerable percentage of magnesia, which seems to be interchangeable with lime and to replace the latter without disadvantage.

The kilns used for burning natural cement are very similar to those used for burning lime. The best kiln consists of a steel cylinder lined with firebrick and provided with an opening at the bottom through which the burned material may be drawn from the kiln. The kiln is continuous in operation and the charging is done by introducing at the top alternate layers of limestone and fuel. This latter usually consists of small-size anthracite coal or coke. The temperature of burning is usually between 1000° and 1200° C. (See Figure 5, p. 867.)

After passing through the kilns the burned material presents the appearance of a soft yellowish-brown mass. It is then ground to a fine powder. As it is quite soft, this is usually done with buhr-stones or in tube mills. However, excellent results can be obtained by grinding the natural cements to an extreme degree of fineness with some of the more modern mills. The grinding of the clinker should be such that 90 per cent will pass through a 100-mesh screen.

Natural cement is not now used for concrete as its strength is far lower and its hardening much slower than Portland cement. It is used to some extent for laying brick and stone and as a component of cements used for this purpose. Generally some hydrated lime is added to such a mixture in order to give plasticity, and if some Portland cement is also added the mixture will give a stronger mortar. It is also desirable to add some (1 or 2 per cent) waterproofing agent such as stearic acid or calcium stearate.

Portland Cement—*Composition.* Investigations on the composition of Portland cement indicate that this is a mixture of tri-calcium silicate ($3CaO \cdot SiO_2$), tri-calcium aluminate ($3CaO \cdot Al_2O_3$), and di-calcium silicate ($2CaO \cdot SiO_2$). The most important of these compounds is the tri-calcium silicate and the more of this which is present the better, although the other compounds also have hydraulic value. Most Portland cement has its silica about equally divided between the tri-calcium silicate and the di-calcium silicate. All the alumina is present as tri-calcium aluminate and practically all the lime is combined with the silica, alumina and iron. Cement which is sound contains only a trace of free lime. When cement is burned, the CO_2 is first driven off the limestone. The first compounds formed are the $5CaO \cdot 3Al_2O_3$ and the $2CaO \cdot SiO_2$. These then gradually unite with the remainder of the CaO to form $3CaO \cdot Al_2O_3$ and $3CaO \cdot SiO_2$, some $2CaO \cdot SiO_2$ remaining in excess. The iron oxide present in ordinary cement acts as a flux and promotes this change.

There is a definite relation between the possible composition of Portland cement and the conditions under which it is made. By finely grinding the raw materials, burning slowly and having the composition sufficiently high in lime, cements with a high percentage of tri-calcium silicate can be made. These, when finely ground, will be quick hardening and show great strength. The so-called "high-early-strength" cements are obtained by this means.

Knowledge gained from the use of the phase rule and phase rule diagrams has done much to produce a better Portland cement and one of uniform quality. The phase diagram[1] for the system lime-alumina-silica is shown in Figure 1. The most desirable constituent of cement, tri-calcium silicate, is designated on this diagram as C_3S. It will be noted that the field for this compound is very small, which means that it exists over only narrow ranges of composition of the mix. The smallness of this field of permissible composition is a challenge to the cement industry, for it calls for very close control of composition and operating conditions to obtain the desired constituent. In recent years the industry has been very successful in meeting this challenge, as evidenced by greatly increased quality and reliability of cement.

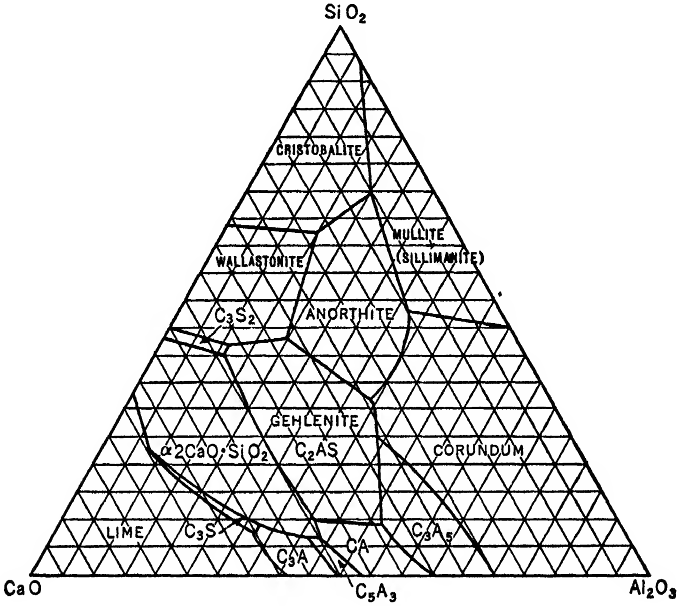

FIG. 1. Phase Diagram of the System $CaO—Al_2O_3—SiO_2$.

Iron oxide is also present in cement, so the phase diagram should really be for four components. But in the quantity in which iron oxide occurs in the raw materials it does not greatly affect the size or position of the fields of composition so the three-component diagram is valid for the control of cement manufacture.

The chemical composition of Portland cement of good quality is usually within the following limits:

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[1] For detailed explanation of the meaning of such diagrams see: Taylor, H. S., "A Treatise on Physical Chemistry," second edition, Vol. I, Chapter IX, Van Nostrand (1931).

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RANGE OF COMPOSITION OF PORTLAND CEMENT

	Limits	*Average*
Silica	20-24%	22.0%
Iron oxide	2-4	2.5
Alumina	5-9	7.5
Lime	60-64.5	62.0
Magnesia	1-5	2.5
Sulfur trioxide	1-2	1.75

Analyses of typical Portland cements are reported in Table 3.

TABLE 3—ANALYSIS OF PORTLAND CEMENTS *

Where Made	*Made from*	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	*Loss*
New Jersey	Cement rock and limestone	21.82	2.51	8.03	62.19	2.71	1.02	1.05
Pennsylvania		21.94	2.37	6.87	60.25	2.78	1.38	3.55
Michigan	Marl and clay	22.71	3.54	6.71	62.18	1.12	1.21	1.58
Ohio		21.86	2.45	5.91	63.09	1.16	1.59	2.98
Virginia	Limestone and clay	21.31	2.81	6.54	63.01	2.71	1.42	2.01
Missouri		23.12	2.49	6.18	63.47	0.88	1.34	1.81
Pennsylvania †		23.56	0.30	5.68	64.12	1.54	1.50	2.92
Illinois	Blast furnace slag and limestone	22.41	2.51	8.12	62.01	1.68	1.40	1.02
Germany	....	20.48	3.88	7.28	64.03	1.76	2.46	
Belgium	....	23.87	2.27	6.91	64.49	1.04	0.88	
France	....	22.30	3.50	8.50	62.80	0.45	0.70	
England	....	19.75	5.01	7.48	61.39	1.28	0.96	
Germany ‡	Iron ore and limestone	20.5	11.0	1.5	63.5	1.5	1.0	

* From Meade's "Portland Cement." † White Portland cement. ‡ Sea-water cement.

As indicated above, the essential elements in cement are lime, silica and alumina. The magnesia comes from the limestone, some of this being present in all limestone. The amount is limited by the standard specifications to 5 per cent, as it is supposed to be harmful. Iron oxide is present in nearly all clays and shales, and hence is always present in cement. It has a definite advantage, in that it assists in burning and lowers the temperature of fusion. Cement containing no iron is white, but rather hard to burn. The sulfur trioxide for the most part comes from the gypsum which is added to correct the set.

The proportions of a good cement should satisfy the following ratios:

$$\frac{\text{Per cent lime}}{\text{Per cent silica} + \text{per cent iron oxide} + \text{per cent alumina}} = 1.9 \text{ to } 2.15$$

$$\frac{\text{Per cent silica}}{\text{Per cent alumina}} = 2.5 \text{ to } 4.$$

In the manufacture of Portland cement great care is taken to see that the composition satisfies the above ratios. If too much lime is present the cement will be "unsound"—that is, in time concrete made from it will expand and crack. If too little lime is present the concrete will be low in strength and may "set" quickly—that is, harden before the masons have a chance to place it in the forms. Cement in which alumina is high is also apt to be quick setting, and is hard to burn uniformly. High silica cements are usually very slow hardening, and do not attain their full strength for a considerable period.

METHODS OF MANUFACTURE

Materials—The materials from which Portland cement is manufactured may be divided into two classes: those which supply the lime and those which supply the silica, iron oxide and alumina. The first are termed calcareous and the second argillaceous. The following groups show the principal materials used in the manufacture of Portland cement.

Calcareous Materials		*Argillaceous Materials*
Limestone	Cement Rock	Clay
Marl		Shale
Chalk		Slate
Alkali waste		Blast furnace slag

The cement rock is an argillaceous limestone which contains usually between 65 and 80 per cent calcium carbonate. If it contains more than 75 per cent it is necessary to add clay, shale or slate in order to make a satisfactory mixture for burning. If it contains less than 75 per cent it will be necessary to add limestone for a similar purpose.

Limestone is usually mixed with clay or shale; marls and chalks with clay. Blast furnace slag is used with limestone. Alkali waste (or precipitated $CaCO_3$, obtained from the manufacture of caustic soda) is mixed with clay.

Limestones, marls and chalks which are to be used in the manufacture of Portland cement should contain less than 3⅓ per cent magnesia and preferably not more than 3 or 4 per cent silica, iron oxide and alumina combined. Clay, shales and slates should all have at least 2½ and not more than 4 times as much silica as alumina. Exceptions to this are in the case of a high silica limestone, with which a high alumina clay may be used to advantage, since all that is necessary is that the mixture shall satisfy the requirements expressed by the above formulas for the desirable composition.

In rough outline the manufacture of cement consists of mixing the calcareous and argillaceous materials together intimately and heating them to the point of incipient fusion. The intimate mixing of the two materials is accomplished by finely grinding them together. The fine powder is then subjected to a temperature of from 1400° C.-1600° C., when a sintering or semi-fusion takes place and the mixture rolls up into little balls varying in size from that of a walnut down to that of wheat, with an occasional larger piece and some fine sand. After cooling, these lumps or "clinkers" are mixed with a small amount (2-3 per cent) of gypsum and finely pulverized. The resulting powder is Portland cement.

Two Processes—The two processes employed for the manufacture of cement are known respectively as the *wet process* and the *dry process*. The wet process is the older of the two and is used almost universally in Europe. The dry process originated in America and is employed to the greater extent here. The two processes differ only in the treatment of the raw materials and very much the same equipment is used in each. The treatment of the burned clinker is the same in both cases.

The wet process is always used for marl and clay and the dry process for cement rock and for blast-furnace slag. Both processes are used for limestone and clay or shale. Where applicable, the dry process is the more economical but it is easier to control the composition of the cement by the wet process. This latter is also better where the materials cannot easily be dried.

Where the wet process is employed for limestone and shale, the two materials are crushed and stored without drying just as in the dry process. They are then mixed in proper proportions and fed to the grinding machinery, at which point water is added and the materials ground wet. The result is a thin mud or "slurry," as it is called, which is made just fluid enough to flow easily. This slurry, containing from 35 to 40 per cent water, is fed directly into the kilns and burned.

In the dry process, the limestone, cement rock, and shale are usually crushed to about two inches or smaller and then dried. The crushing is nearly always done in large jaw or gyratory crushers which are followed by hammer mills. The dried materials are stored in separate bins or piles and are drawn out of these as desired and mixed in proper proportions by automatic scales. The mixture is then ground and burned. Sometimes the storage and mixing precede the drying.

Drying is done by means of rotary driers. These are cylinders of sheet steel from 6 to 8 feet in diameter and from 60 to 100 feet in length. They are unlined, and are usually provided with channel irons bolted to the inside to act as shelves, to carry the rock up and drop it through the hot gases. The driers are heated by a coal fire at the lower end or else by the waste gases from the rotary kilns. They are similar in construction to the rotary kilns described farther on except that they are smaller and are not lined with firebrick.

Storage—In order to provide a constant supply of material in case of a cessation of quarry operations, due to bad weather, etc., a storage is usually provided for the crushed raw material. This is often sufficiently large to hold a week or two's supply of material. The most common form of storage is large covered concrete bins provided with belt conveyors—one overhead for bringing in the stone and others in tunnels underneath the bin for taking it out. Another form of storage is provided with a traveling crane and grab bucket, similar to the storage for clinker which will be described further on.

Mixing—The materials are usually mixed after leaving the storage, various methods being employed for proportioning the two different kinds. Hopper scales are used in many of the older mills, while in most of the newer ones limestone and shale are proportioned just as they are fed to the grinding mills by means of some type of adjustable feeder such as a "poidometer" or a rotating table feeder. Clay is often first worked up with water and the thin slip formed is proportioned by volume to the limestone just before the latter goes to the ball mill or compeb mill. A revolving wheel with wickets, known as a Ferris wheel, is usually employed for this purpose.

Where the wet process is employed for limestone and shale or clay, no drier is employed and sufficient water to make the ground material flow is added just before the mill.

Grinding—The grinding of the raw materials may be done in one or in two stages. The combinations now most often employed are (1) Ball mill and tube mill, (2) Kominuter and tube mill, (3) Hercules mill and tube mill, (4) Griffin mill and tube mill.

In place of the combination of ball and tube mill, a single mill combining the elements of these two mills is now most generally used in the newer cement plants. These combination mills go under different names according to the maker such as "Compeb Mill," "Unidad Mill," "Combination Mill," etc. These mills are somewhat similar to a tube mill except that they are made longer and there are usually three or more compartments, separated by perforated or grid partitions.

The degree of fineness to which the raw material is to be ground depends entirely upon conditions. It is stated as a general rule that it should be sufficiently fine so 90 per cent will pass through the 100-mesh sieve, and in most cases 95 to 98 per cent is required to produce a sound cement. The finer the grinding the more perfect the combination between the silica, the alumina, the iron and the lime during the burning operation. If the raw materials are not finely enough ground, the cement will be unsound—that is, some of the lime will not combine. This yields a cement which disintegrates rapidly.

Flotation—The fine grinding of the cement materials affords the possibility of the use of a unique method for adjusting the composition of the mix. As has been indicated above, the various oxides must be proportioned within fairly narrow limits to give a satisfactory product. This means that many deposits of natural materials cannot be used because they cannot be proportioned in any way to give the desired chemical composition. Recently the operation of flotation has been used with great success to separate the finely ground mineral constituents from each other.[2] It is now being used to correct mixtures and to make many raw materials usable which were formerly considered unusable. By removing impurities from cheap materials they can be used to replace the more costly ones. Proper control of the flotation operation produces a better mix before burning. This has been one of the principal developments in the cement industry in recent years.

(For a general discussion of the operations of crushing, grinding and flotation, see Chapter 2, The Unit Operations.)

Storage of Ground Material—In the wet process, the ground materials containing from 33 to 40 per cent water, are stored in tanks or basins which are agitated with either mechanical or compressed air agitators. The material as ground is usually passed into one set of vats called correction basins from which samples of the slurry are drawn and analyzed. When a basin is full, if the composition is not correct, it is adjusted either by stirring in more clay or by mixing the contents of two or more basins. The slurry whose composition has been satisfactorily adjusted is then passed on to a second set of basins known as "kiln feed basins." These are also provided with agitators.

In the dry process, it was quite usual at the older plants to send the material directly from the grinding mills to the kilns. At the newer plants, however, the ground material is sent into large storage tanks where its composition is

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[2] Engelhart, G. K., Ind. Eng. Chem. *32*, 645 (1940).

checked and if found unsatisfactory is adjusted by blending the contents of two or more tanks, etc. When this is done the dry process will give fully as uniform cement as the wet.

Conveying Materials—The material is usually carried from one stage of manufacture to another by various types of conveyors. The product of the crushers is conveyed to the granulating mills on belt conveyors, and the product of these latter mills and the tube mills is transported by screw-conveyors. The elevating is done by means of bucket elevators of the link-belt type. Finely ground raw material and cement may also be conveyed by means of the Fuller-Kinyon system through a pipe line. Slurry and marl are pumped through pipe lines by means of either plunger or centrifugal pumps, or by a compressed air system.

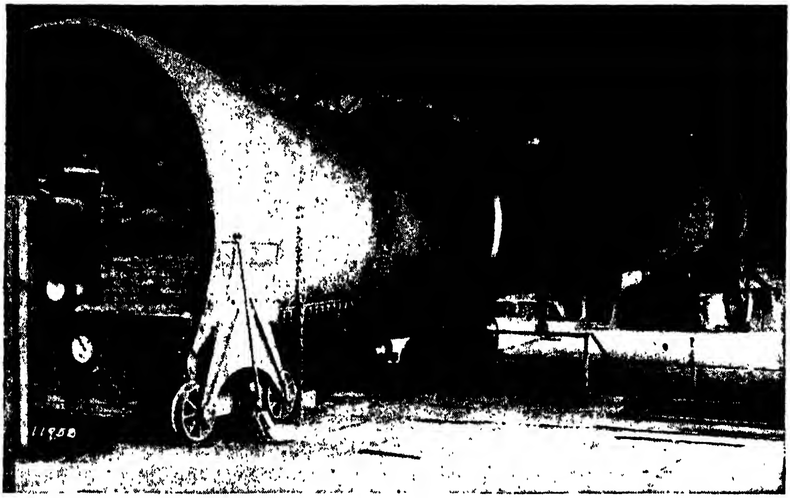

Fig. 2. Rotary Cement Kiln—View from Firing End.

Burning—In the early days of the American Portland cement industry, the burning was done in intermittent upright kilns, similar to those used for burning lime. These were soon improved, by making them continuous in action in order to economize on fuel. This allowed the charge to receive the waste heat from the clinkering of the cement, and the air for combustion to be preheated, by passing through the fully-burned material.

The Rotary Kiln. The rotary kiln was introduced about 1887 and this is the form of kiln now universally used in this country.

The rotary kiln, in its usual form (Figure 2), consists of a cylinder, from 6 to 12 ft. in diameter and from 60 to 350 ft. long, made of sheet steel and lined with firebrick. The burning of cement is essentially an application of the unit operation of heat transfer, by radiation, and therefore it is necessary to have equipment and conditions which will bring about a large amount of heat transfer[3] from the flame to the solid material.

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[3] For a discussion of the factors which contribute to rapid heat transfer by radiation, see Chapter 2.

The steel sheets of the kiln are held together by single-strap butt joints. This long cylinder is supported at a very slight pitch (½ to ¾ in. to the foot) from the horizontal, on two or more tires made of rolled steel, which in turn revolve on heavy friction rollers. The kiln is driven at a speed of from one-half to one revolution per minute by a girth-gear situated near its middle, and a train of reducing gears. The power is supplied by either a line shaft or a motor. The upper end of the kiln projects into a brick flue, which is surmounted by a steel stack, also lined with firebrick for its entire height. The flue is provided with a door at the bottom, which serves not only to allow the flue to be cleared of the dust which accumulates in it, but also a damper to control the draft of the kiln.

The material to be burned is usually fed into the kiln through a horizontal water-jacketed screw-conveyor, or else spouted into it through an inclined cast-iron pipe. The raw material feeding device is usually attached to the driving gear of the kiln, so that when the kiln stops the feed also stops.

The lower end of the kiln is closed by a firebrick hood. This is usually mounted on rollers, so it can be moved away from the kiln when the latter has to be relined. The hood is provided with two openings: one for the entrance and support of the fuel-burning apparatus, and the other for observing the operation, temperature, etc., of the kiln, and through which bars may be inserted to break up the rings of material which form, and to patch and repair the lining. The lower part of the hood is left partly open. Through this opening the clinker falls out and most of the air for combustion enters.

Typical capacities of various sizes of rotary kilns are given in Table 4.

TABLE 4—CAPACITIES OF ROTARY KILNS—BBLS. PER DAY

	Dry Process	*Wet Process*
6-ft. diam. × 60 ft. long	200	140
7-ft. diam. × 100 ft. long	430	300
8-ft. diam. × 125 ft. long	700	500
9-ft. diam. × 150 ft. long	1100	800
10-ft. diam. × 175 ft. long	1500	1000
11-ft. diam. × 175 ft. long	2000	1500
11-ft. diam. × 250 ft. long	2500	1800

Heating the Kiln—The kiln is heated by a jet of burning fuel, usually powdered coal, but sometimes natural gas or fuel oil are used.

The necessary temperature of the hottest part of the kiln is about 1400° C., and is rarely less than 1300° C. To maintain this temperature, about 80 lbs. to 160 lbs. of fuel are required per barrel of cement, the actual amount depending on the coal itself, the material to be burned and the dimensions of the kiln. The longer the kiln, the greater the fuel economy. Dry materials require much less coal than slurry. With limestone and shale mixture, in a kiln 100 ft. long by 7 ft. in diameter, the coal consumption will amount to about 90 lbs. of good gas slack per barrel. A kiln 60 ft. long by 6 ft. in diameter will, on the other hand, require about 110 lbs. of coal per barrel. Wet materials require about 30 per cent more fuel.

Grinding the Coal. When coal is used for burning, this is pulverized in mills similar to those used for grinding the raw materials. It is, however, first crushed by passing through rolls or roll-jaw crushers, and then dried in rotary driers of special type. The mills most used for coal pulverizing are the Fuller mill and the Raymond mill. The coal should be pulverized so that 90 per cent of it will pass a sieve having 100 meshes to the linear inch, and should contain from 30 to 45 per cent volatile matter.

Thermal Efficiency. Of the heat supplied to the kiln by the burning of the coal, by far the larger proportion is wasted. About 50 to 75 per cent of it is carried off by the waste gases of the stack, and from 10 to 15 per cent by the hot clinker falling from the lower end of the kiln. The gases enter the stack at from 600°-800° C., and the clinker leaves the kiln at not much under 1200° C. If the kiln could be made to show the same economy as is common in good boiler practice, a barrel of cement could be burned with 25 lbs. of coal.

The gases leave the dry process kiln at about 800° C. In many plants the waste gases are led through waste heat boilers located at the end of the kilns. By so doing about 4 to 5 lbs. of steam are generated per pound of coal burned. The flow of gases through the boilers at a high velocity is one of the requisites for successful employment of the waste gases for steam generation and this is obtained by means of an inducted draft fan. By employing modern turbine engines, directly connected to electric generators, enough power may be obtained from the waste gases to operate the entire plant. The gases are sometimes purified and the carbon dioxide reclaimed.

Dust Losses. Normally from 3 to 5 per cent of the raw material is carried away in the exit gases of the kiln as dust. Various schemes have been tried with a view to eliminating the dust, such as settling chambers, water sprays and electrical precipitation. The latter, Cottrell precipitator, is the only method, however, which is used to any extent. Several installations of this system are now in operation. The dust collected by the latter is found to contain considerable potash for about half the potash in the raw material is volatilized in the kiln. Some of this potash is water soluble and may be recovered and used for fertilizer.

Forming the Clinker. The raw material as it enters the kiln contains about 33 per cent carbon dioxide. For the first 30 ft. of its journey through a 100-ft. kiln, it is merely heated up, and whatever water it contains is driven off. In the next 40 ft. it loses all its carbon dioxide and sticks together, forming small, soft, lemon-yellow balls, which, as they reach the hottest part of the kiln—the last 30 ft.—partially vitrify, become rough and hard. Properly burned Portland cement clinker is greenish-black in color, of vitreous luster, and, usually, when just cooled, sparkles with small bright glistening specks. It forms in lumps from the size of a walnut to hardly more than dust, with here and there a larger lump. Under-burned clinker is more or less soft, is irregular in shape, and not as black as the well-burned material. It usually shows soft-brown centers. Hard-brown centers are due to very hard burning.

Cooling the Clinker. As the clinker leaves the kiln at about 1200° C., it is entirely too hot to grind, and must be cooled to ordinary air temperatures. This can be done by allowing it to lie in piles or by passing it through revolving coolers. The latter consist of steel cylinders provided with angle irons on the inner periphery to carry the material up and drop it through the current of air passing through the cylinders. They are mounted on tires and rollers, just as are kilns and driers, and revolve at one or two revolutions per minute. They are usually placed below the kiln, and the clinker falls into them from the kiln. The air for cooling is also drawn through them into the kiln. They thus serve not only to cool the clinker but also to preheat the air entering the kiln.

When the clinker is cooled in piles it is usually handled by means of bridge cranes equipped with grab buckets of the clamshell type. Cooling out of doors by this method also serves to season the clinker. This makes it easier to grind and also makes it sounder, due to the slaking of any free lime present in the clinker. A modern plant will employ a bridge crane operating on an elevated track and covering an area sufficient for 100,000 to 300,000 bbls. of cement.

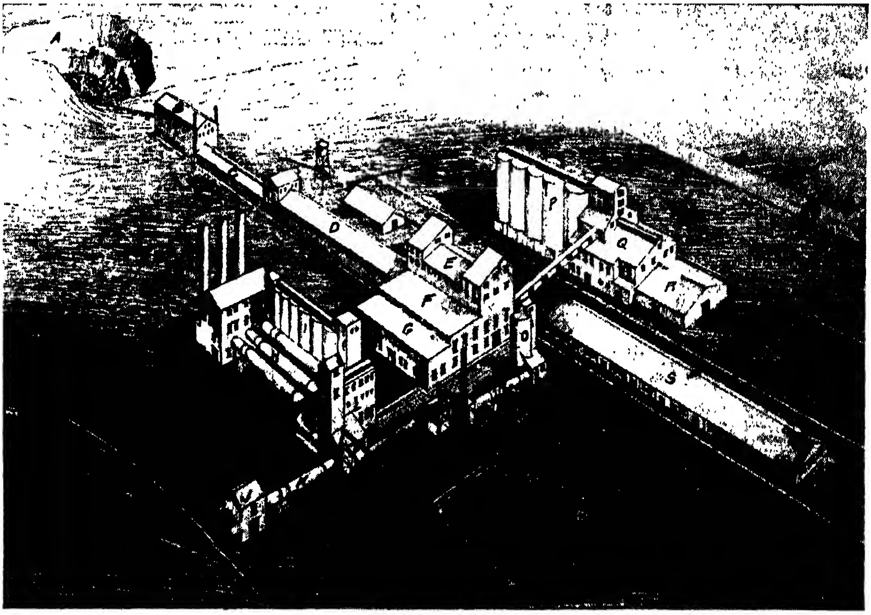

Fig. 3. Bird's-eye View of a Modern Cement Plant.

Grinding the Clinker. After cooling, the clinker is ground, in any of the mills previously mentioned, to a fineness of at least 78 per cent, passing a sieve having 200 meshes to the linear inch.

In order to regulate the set of the cement, since clinker ground alone would set very rapidly, it is necessary to add 2 to 3 per cent of calcium sulfate to it, usually as gypsum, or plaster of Paris. It is the usual practice to add the retarder to the clinker before the latter is ground, and to grind the two together.

Storing the Clinker. After passing through the clinker mills, the cement is conveyed to the stock house. This consists of a number of reinforced concrete silos similar to those employed for storing grain. They are each from 25 to 35 ft. in diameter and from 50 to 80 ft. in height. A modern cement plant will usually have storage for at least a three-month output. Stock houses of from 100,000 to 250,000 bbls. capacity are quite common.

The cement is brought into the stock house by an overhead conveyor or the Fuller-Kinyon system pipe line and dropped into any desired bin. A screw-conveyor also runs under the floor of the stock house. The bins are provided with gates, and when it is desired to pack from any bin, these gates are opened and the cement is allowed to run into the screw-conveyor. The screw-conveyors then carry it to the packing machines.

Cement is packed almost exclusively in paper or cloth bags holding 94 lbs. each, 4 bags constituting a barrel (376 lbs. net). The cement is packed as shipped, and the bags are trucked directly to the cars.

Figure 3 is a bird's-eye view of a modern cement plant.

CONCRETE

When Portland cement is mixed with water and sand or fine aggregates, it is called mortar. If coarse aggregates, such as crushed stone or gravel, are used in addition, the mixture is then referred to as concrete. A fine aggregate in concrete should be ⅛" to ¼" in diameter, while the coarse aggregate should run from ¼" to 1½" in diameter. The proportion of cement, sand and aggregates in concrete varies with the use to which it is to be put. Concrete for watertight work is made up of one part cement, one part sand and two parts gravel. If not required to be watertight, the mixture can be changed to one part cement, three parts sand and five parts gravel. The more cement, within limits, the more waterproof the concrete will be. In addition, concrete must be cured and the slower dried, by keeping the mixture damp, the better the concrete and the more waterproof. Slow drying and a larger amount of cement permits the voids in the aggregate to be filled, thereby producing a better concrete. Curing is retarded by low temperatures but freezing should be avoided as this impairs the strength of the finished material. When concrete is placed around iron or steel rods and around various structural shapes the resulting mass is referred to as reinforced concrete.

PUZZOLAN CEMENTS

Puzzolan cements are of very ancient origin, and in most of the engineering work done by the Romans this cement was employed. They manufactured it by mixing slaked lime with fine volcanic ash. These cements are still employed to some extent in Europe, but have never found a market in this country. A cement manufactured from blast furnace slag and slaked lime was made at one time in this country by a number of concerns, but at the present time its manufacture has been almost entirely discontinued. Its only use now is for a non-staining cement for laying tile. The activity of this class of cement depends upon the fact that the volcanic ash and slag both contain soluble silicic acid, which readily enters into combination with calcium hydrate to form silicates.

In manufacturing slag cement, the cement is chilled and granulated by running it, while still molten, into water or by directing a stream of water against a stream of melted slag. This slag is then mixed with slaked lime and very finely ground. Slag cement must not be confounded with Portland cement made from slag. Several new forms of slag cement have recently been introduced. These consist in granulating slag of proper composition with water and mixing the slag so obtained with a small percentage of Portland cement clinker. The

"Passow Cement," manufactured in Germany, is of this class. A mixture of 30 per cent granulated blast furnace slag and 70 per cent Portland cement is marketed in Germany under the name "Iron Portland."

LIME

Lime is nearly pure calcium oxide, CaO; or a mixture of calcium and magnesium oxides, CaO + MgO; sometimes called quicklime. High calcium limes are stronger than those containing considerable percentages of magnesia. They are also better suited for mortar work, as they slake more readily. Magnesium limes, on the other hand, are better for plaster finishing because they work more smoothly under the trowel. Pure lime, whether magnesium or not, is snow white. However, a very small percentage of certain impurities such as iron or manganese may give the lime a gray or yellow color. Through certain methods of burning the ash of the fuel may be introduced into the lime, causing discoloration. Typical analyses of raw materials used for lime production are given in Table 5.

TABLE 5—ANALYSIS OF MATERIALS USED FOR MANUFACTURE OF LIME AND CEMENT

Material	*From*	SiO_2	Fe_2O_3 Al_2O_3	CaO	MgO	CO_2	SO_3	*Used for*
Limestone...	Annville, Pa.......	0.36	0.45	54.45	0.54	43.24		Portland cement
Limestone...	Glens Falls, N. Y...	3.30	1.30	52.15	1.58	40.98		"
Limestone...	Mitchell, Ind......	0.74	0.13	52.94	1.87	43.68		
Marl........	Bronson, Mich.....	1.78	1.21	49.55	1.30	40.35		"
Cement rock.	Nazareth, Pa......	13.44	6.60	41.84	1.94	32.94		"
Cement rock.	Martin's Creek, Pa.	11.11	6.31	42.51	2.89	36.57		
Clay........	Alpena, Mich......	61.09	26.97	2.51	0.65	......	1.42	"
Clay........	Suisun, Cal........	58.44	26.50	1.70	1.88	......		"
Cement rock.	Rondout, N. Y.....	15.37	11.38	25.50	12.35	34.20		Natural cement
Limestone...	Union Bridge, Md..	0.89	0.47	54.68	0.32	43.44		Lime
Limestone...	Woodville, Ohio...	0.78	0.48	31.15	20.78	45.76		"
Oyster shells.	Long Island Sound.	3.30	0.25	52.14	0.25	41.61		"

Lime is made by burning limestone in suitable furnaces at a temperature sufficient to drive off all of its carbon dioxide, the reaction being:

$$CaCO_3 + 21{,}900 \text{ cals.} \rightleftharpoons CaO + CO_2.$$

Theoretically, 806 gram-calories per gram of calcium oxide and 733 gram-calories per gram of magnesium oxide are required to produce this change. At atmospheric pressure the temperature at which calcium carbonate decomposes[4] is stated as 898° C., while magnesium carbonate decomposes at 575° C.

Kilns—Lime kilns are ordinarily operated at from 900° to 1100° C. in the hottest or burning zone. If a temperature much above 1200° C. is employed,

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[4] Johnston, J., J. Am. Chem. Soc. *30*, 1357 (1908).

the lime will be partially vitrified on the outside of the lumps, due to combination of the CaO with impurities SiO_2 and Al_2O_3, always present in small quantities in even the purest limestone. This causes the lime to be very slow in slaking, which is undesirable, as some of it may escape hydration in the mortar box and later will expand, or "blow" or "pop" in the wall. This manifests itself in small blisters in the finished plaster work.

Intermittent Kilns. The types of kilns ordinarily employed in burning lime may be divided into two classes—intermittent and continuous. The intermittent kilns are primitive and uneconomical, though they are frequently used by farmers and other small producers of lime. Figure 4 shows such a kiln. There is a great waste of heat and time in such a kiln, owing to the fact that it must be cooled and reheated each time it is charged. They are seldom, if ever, used in large scale commercial operations.

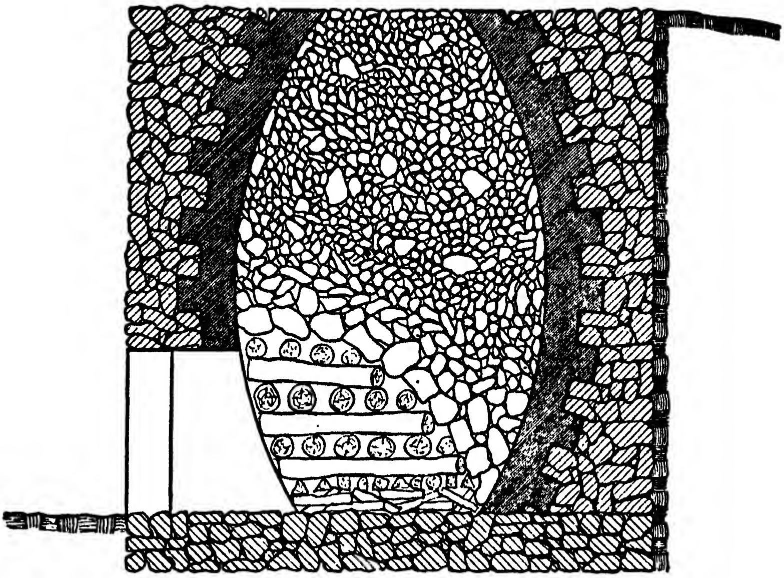

FIG. 4. Intermittent Type of Lime Kiln.

Continuous Kilns. Three different types of continuous kilns are employed: these are, (1) the vertical kiln with mixed feed, in which the limestone and fuel are charged in alternate layers; (2) the vertical kiln with separate feed, in which the limestone and fuel are not brought in contact; and (3) the rotary kiln.

Vertical Kiln, Mixed Feed. Vertical kilns with mixed feed are similar to the intermittent ones, except that they are provided with an arrangement whereby the lime may be drawn at regular intervals from below. They are built on the side of a hill, usually of limestone blocks, and are sometimes lined with firebrick. In charging them, first a layer of anthracite coal or coke and then a layer of limestone is fed into the top. Fire is started at the bottom and works its way up. The process of charging and drawing the lime is continuous. These kilns are economical and, for the same size kiln, yield a larger quantity of product than do the vertical kilns with separate feed. On the other hand, the lime is contaminated by ash of the fuel, and the lime burned in these kilns must be carefully sorted in order to discard those lumps to which the fuel ash has adhered.

Vertical Kiln, Separate Feed. The vertical kiln with separate feed usually consists of a steel cylinder lined with firebrick. This is equipped with two or four fireplaces for the burning of the fuel, which are built into the sides of the kiln, so that the fuel is not mixed with the stone. The hot gases of combustion pass from the fire-box into the kiln, while the ash of the fuel drops through the grate bars into an ash-pit below, and does not mix with the lime. The kilns are often constructed with a hopper-shaped cooling chamber, set below the fire-box, which is closed by doors at the bottom. The cooling chamber holds about one draw of lime. Figure 5 shows such a kiln. They are from 6 to 10 ft. in cross-section, and from 40 to 50 ft. in height. They are usually charged by employing an incline and a cable hoist, by means of which the cars of limestone are drawn from the quarry to the top of the kilns. They are sometimes provided with steel stacks in order to induce a better draft.

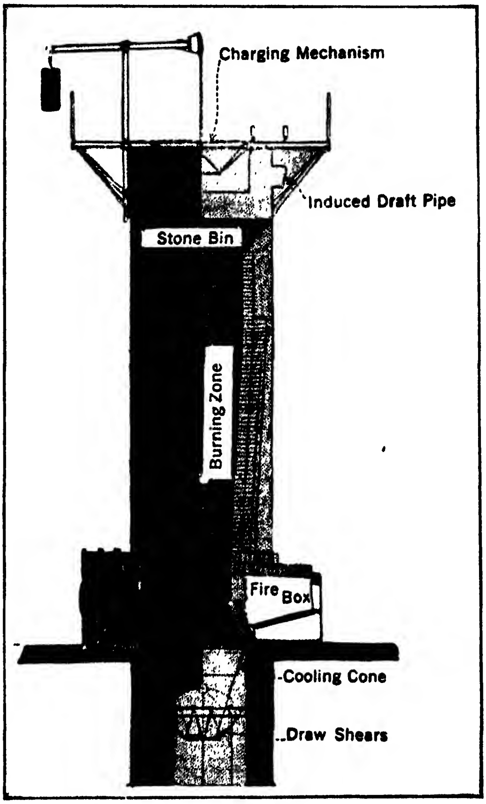

FIG. 5. Vertical Type Lime Kiln.

An improved system of draft employs an exhauster. Where this is done, it is of course necessary to close the top of the kiln and to charge the limestone into the latter through a door or a charging bell somewhat similar to that of a blast furnace. Figure 5 shows such an arrangement. When the kiln gases are drawn off for their carbon dioxide (as in the Solvay process for soda) this bell type of seal is generally employed. A properly installed induced draft will often increase the capacity of a kiln 50 per cent.

Wood, oil, and coal are employed for burning the wood. Wood is the best fuel, as it burns with a long flame of comparatively low temperature. This is an advantage, as it is essential that the heat should be dispersed a considerable distance throughout the kiln without having excessive temperatures at the mouth of the fire-box. The steam, which the wood introduces, also seems to be beneficial, and indeed some manufacturers prefer to use green wood because of the greater quantity of steam which it introduces. Wood-burned lime is whiter than that burned with coal.

Where coal is employed as a fuel, it is customarily used wet. A steam jet is also often employed, being inserted below the fire-box. The steam passing through the hot bed of coals is decomposed into hydrogen and carbon monoxide as follows:

$$H_2O + C = H_2 + CO.$$

These gases are burned in the kiln itself, and hence carry the heating zone further up the shaft.

With hand-fired kilns the diameter cannot be increased beyond the limit to which the flames from the fire-box can reach effectively or the limestone in the center of the kiln will not be burned. The limiting diameter for such a kiln is about 6 to 7 ft. With gas, on the other hand, the kiln may be made much larger because the gas may be made to burn in all parts of the kiln. The use of gas also saves the labor of stoking the grates. On the other hand, more skill is required to burn lime with gas than with any other fuel and considerable experimenting is usually required before satisfactory results are obtained. Natural gas is used and producer gas[5] is now being used for kilns of large capacity. Usually the producer gas enters through openings around the side of the kiln and the air through holes in the bottom of the kiln. The air is thus preheated by passing up through the hot lime, which it cools. It then comes in contact with the producer gas in the center of the kiln, where combustion takes place, spreading back to the gas openings. Gas-fired lime kilns are now built having capacities of from 40 to 60 tons per day.

Oil also makes an excellent fuel. When it is used in the kiln described, the burner is placed in the door openings of the fire-boxes and these are bricked in with firebrick leaving openings for the burner and for observing the lime.

The shaft kilns described above when heated with wood, coal, or oil will produce from 8 to 20 tons of lime per day, depending on the kiln and the limestone burned and whether natural or induced draft is employed. When fired with gas the capacity will range from 17 to 60 tons per day.

Rotary Kilns. Lime is also burned in rotary kilns similar to those described in the section on Portland cement. The limestone is first crushed to pieces ranging in size from 2½ ins. down to dust and fed into the kiln, which is heated by producer gas, oil or powdered coal. These kilns are peculiarly adapted to burn-

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[5] For a discussion of making producer gas see Chapter 19.

ing highly crystalline stone, which would crumble when subjected to heat and so stop the draft of the vertical kiln, and to supplying lime for chemical and metallurgical purposes.

There was at one time considerable objection to the use of rotary kiln lime, due to small particle size produced. The mason, being accustomed to lime in large lumps, assumed the rotary kiln lime was air-slaked. Now, however, this prejudice has been overcome and much lime is sold in the powdered or granular condition. Powdered lime, made by grinding lump or granular lime which results by decrepitation when certain crystalline limestones are burned, slakes much quicker and is less likely to pit than are most lump limes. Pebble lime is a rotary kiln lime made by burning carefully sized stone usually ranging between 1 to 2½ ins. Better results are obtained as regards the uniformity of the lime if material finer than ¼ in. is screened from the stone before burning.

The rotary kiln is more economical of labor than is the shaft kiln. This applies to both the quarry, where stone for the latter must be carefully sized and all small stones discarded, and to the attention required by the kiln itself. It requires more fuel than the best type of shaft kiln, but the heat in the stack gases may be recovered by installing waste-heat boilers after the kilns, passing the waste gases through the boilers and utilizing the steam for power, etc. Rotary kilns are now being quite generally employed for burning building lime where a large output is required. A kiln 8 ft. diameter by 150 ft. long will produce 100 tons or more per day.

Rotary kilns are also used to burn lime from various wastes, such as "lime-sludge" from paper mills and sugar purification. Lime is now burned from the calcium carbonate waste from caustic soda manufacture[6] at a number of plants by first passing the waste through some form of dewatering device such as a continuous rotary, drum or disc filter, the waste being obtained from the latter in the form of a wet mud containing about 50 per cent water. The recovered lime is very pure and usually contains some alkali otherwise lost, the percentage varying from 3 to 8 per cent of the lime recovered. This practice not only can be carried out generally for less than the cost of purchasing lump lime but it also disposes of a troublesome waste product.

The rotary kiln is particularly well adapted to burning chemical lime and is to be preferred where a very well-burned lime, free from carbon dioxide, is desired as in the manufacture of carbide and in metallurgy.

A refractory product is now made by grinding together dolomite, $CaMg(CO_3)_2$, and a small amount of iron ore, and burning the mixture in a rotary kiln at a somewhat higher temperature than is required for lime. The product so obtained consists of small roughly rounded nodules, hard and dark brown to black in color. It generally contains from 4 to 8 per cent iron oxide. The function of the latter compound is to make the lime slake less readily on exposure to the air and so improve its keeping qualities. This material is known in the trade as "*dead burned* dolomite" and under various trade names.

Fuel Requirements for Shaft Kilns—The quantity of fuel required depends on many things, among which may be mentioned the kind and quality of fuel, skill of the operator, and the limestone itself. Magnesium limestone burns more

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[6] See Chapter 10.

easily than high calcium stone and an impure stone more easily than a pure one. The amount of fuel actually required is about as follows:

1 ton of good bituminous coal, hand-fired, will burn from 3 to 4½ tons of lime;
1 barrel of fuel oil will burn ⅔ to 1 ton of lime;
1 cord of seasoned hardwood will burn from 1½ to 2½ tons of lime.

Hydrated Lime—When quick-lime is treated with water it combines with the water to form calcium hydroxide:

$$CaO + H_2O = Ca(OH)_2.$$

If the lime is free from impurities, it will take up 32 per cent of its own weight of water. This quantity, however, is reduced somewhat because of the impurities that are always found to a greater or less extent in all commercial limes. When lime slakes, heat is generated. One gram of CaO converted to $Ca(OH)_2$ liberates 270 gram-calories, or enough heat to evaporate 0.5 gram of water at 100° C. The chemical reaction itself requires 0.31 gram of water. Thus, assuming the water and lime both to be at 100° C., 1 gram of CaO could satisfy 0.81 gram of water. In practice appreciably less is employed due to radiation losses, and heat required to bring the materials up to 100° C. Formerly, lime was hydrated, or slaked, by the mason just preparatory to its use. An excess of water was always used, and the calcium hydroxide formed a wet mass called "lime putty." Now, mechanical means of hydration have been introduced whereby the lime is hydrated by the manufacturer with just sufficient water to form the hydrate, leaving none in excess. This hydrated lime is a fine dry powder, practically all of which will pass through a 100-mesh screen. It is packed in paper bags or cloth sacks, and will keep indefinitely. It can be stored without danger of causing fire, which is not true of caustic lime. Mortar made with it shows less danger of blowing or popping in the walls. When added to cement, it makes it waterproof to some extent and more easy to trowel.

In manufacturing hydrated lime the lump lime is first ground to small size. It is then mixed with a predetermined amount of water, when it falls to a fine powder. The slaked lime is then sieved to separate out the unhydrated lumps or siliceous cores from the latter, or else these cores are ground so fine that they will cause no "popping."

The plan adopted in grinding the quicklime in the most successful hydrating plants consists in crushing the lime by means of a swing hammer mill or a Sturtevant open-door crusher. This reduces it to pieces about ½ in. and under. Lime which is to be hydrated should not be burned at as high a temperature as is ordinarily used. Fresh lime hydrates much more readily than that which has been allowed to remain for some time in the air.

There are a number of processes and machines for mixing the lime with water which have been successfully used in hydrating. The four best known of these are the Kritzer, the Schaffer, the Schulthess, and the Clyde hydrators.

Hydrators. The Clyde hydrator is a batch machine, in which a given quantity of lime, usually one ton, is placed. The machine itself consists of a revolving pan provided with plows which store up and mix the water and the lime. The water is weighed and added in a predetermined amount. When the operator judges the process to be complete, as is determined by the fluffiness of the powder, the lime is scraped from the pan through an opening in the center of the same into a hopper under the hydrator.

The Kritzer hydrator consists of a number of cylinders one over the other, which are provided with paddles which revolve around a central shaft. The lime is fed into the upper cylinder in a continuous stream. Here a regulated amount of water is spread upon it. The moist lime is worked by the paddles and passes through the upper cylinder to the next lower one, etc., and finally works its way out at one end of the bottom cylinder. It is now entirely hydrated and dry. The steam from the lower cylinders passes to the upper ones, and helps to hydrate the lime.

In principle of operation the Schaffer hydrator resembles the Kritzer. In its case, however, the working is done by plows in shallow trays which are superimposed one on top the other.

The Schulthess hydrator consists of a stationary horizontal cylinder in the center of which revolves a shaft with plows. The lime is introduced into a revolving screen at one end of the cylinder and water is sprinkled on it here. As it slakes, it falls through the screen and the plows work it through the cylinder. The advantage of this hydrator is that it will handle lumps and hence no crusher is needed.

Hydrated lime is now packed in paper and cloth bags. Automatic machines have been devised which force the lime through a valve in one corner of the bags, which are pasted shut or tied, except for one corner, before the lime is placed in them.

Finishing Lime—Finishing lime is made in the same manner as ordinary lime in a rotary kiln. Dolomite is used, varying in magnesium carbonate content from 10 per cent to 50 per cent. In the United States the dolomite limestone is found in Ohio, New York and a few deposits in the far West. Finishing lime is always supplied to the trade in the slaked form and is called Finishing Hydrated Lime. It is used chiefly as a finishing coat in wall plastering as it gives a very white surface and can be troweled smooth. Another use is as a lubricant in concrete mixtures. Due to the fact that the lime is finer than Portland cement, it acts as a filler and renders the cement watertight. Lime with a high magnesium content has a higher plasticity than other limes.

Hydraulic Lime—Limestones containing amounts of impurities sufficient to give the calcined product hydraulic properties, but insufficient to take up all the lime present, make, when burned, hydraulic limes. They form an intermediate product between ordinary lime and natural cement. These products range from feebly hydraulic limes to limes which harden quite satisfactorily under water. At one time these limes were manufactured to a large extent in Europe. Until recently they were not manufactured in any quantity in this country, but are now made and used to some extent for laying brick and stone. They are generally sold under the designation—"brick cement." They are made by burning limestone containing from 10 to 17 per cent silica, alumina and iron, and from 40 to 45 per cent lime. Magnesia may replace lime to a considerable extent. Hydraulic lime slakes with water just as does ordinary lime, only much more slowly.

Grappier Cements—These are obtained by grinding the hard cores which are obtained in the manufacture of hydraulic lime, and consist of that portion of the hydraulic lime which does not slake when water is added. La Farge cement is of this class, and is imported extensively in this country, owing to its light color and the fact that it does not stain marble and other building stones as does Portland cement and natural cement.

GYPSUM PRODUCTS

Plaster of Paris—Plaster of Paris is sold in the form of a white powder. After being mixed with water it sets very quickly. It is used in art work for casting of figures, in dental work, in making molds, and as a basic material for several plasters. It is made from gypsum by heating the latter to a temperature of between 100° and 204° C., when three-quarters of the water of crystallization of the gypsum is driven off.

$$2(CaSO_4 \cdot 2H_2O) = (CaSO_4)_2 \cdot H_2O + 3H_2O.$$

In actual practice the temperatures employed to bring about this reaction are 165° to 199° C. If gypsum is heated above 204° C., it loses all of its water of combination and becomes anhydrous calcium sulfate, the latter being the basis of hard finish plaster, floor plaster, Keene's cement, etc.

When plaster of Paris is mixed with water it sets or hardens very promptly, this change being due to absorption of water, forming gypsum again.

$$(CaSO_4)_2H_2O + 3H_2O = 2(CaSO_4)2H_2O.$$

A pure plaster of Paris will normally harden or set in from five to fifteen minutes after having been mixed with water. If the gypsum from which the plaster is made contains impurities, the set will be much slower than this. Plaster to be used for building purposes must be slow setting. For ornamental use it must also be white, and since the impurities usually render the plaster slightly colored, it is the common practice to add retarders to the plaster before placing it upon the market. The materials used as retarders are usually of a colloidal nature, such as glue, sawdust, blood, packing-house tankage, etc. Retarders are usually made by digesting hair with caustic soda. If a very quick-setting plaster is desired, crystallized salts are added, such as common salt, sodium sulfate, sodium carbonate, etc.

Gypsum—Gypsum, the raw material from which plaster is made, is, when pure, a hydrous calcium sulfate, $CaSO_4 2H_2O$. As mined, however, it usually contains a considerable percentage of impurities, the chief of which are clay, calcium carbonate and magnesium carbonate. Table 6 gives the analyses of some American gypsums:

TABLE 6—ANALYSES OF TYPICAL GYPSUMS

Locality	SiO_2	Fe_2O_3	$CaCO_3$	$MgCO_3$	$CaSO_4$	H_2O
Nova Scotia	0.10	0.02	1.04	Trace	78.60	20.13
Kansas	0.35	0.12	0.10	0.25	78.73	20.52
Michigan	1.24	0.50	2.38	...	77.19	19.03
Kansas	2.17	0.24	2.66	0.95	75.11	19.40
Oklahoma	17.95	1.43	...	...	61.00	18.44
Oklahoma	10.67	0.60	10.21	1.10	59.46	16.59

Impure earthy gypsum, such as that shown in the last two analyses of the above table, is known in the trade as gypsum earth or gypsite.

Gypsum occurs usually in the form of beds, frequently associated with deposits of rock salt, and almost always interstratified with beds of limestone and shale. The beds, of course, vary greatly in extent and thickness, some of them being as thick as 60 ft., though most of them are very much thinner than this. The principal gypsum deposits found in this country lie in three geological series —namely, the Salina group of the Silurian, the Lower Carboniferous and the Permian. The localities in this country which produce gypsum are central and western New York, south-west Virginia, northern Ohio, Michigan, and a great many of the western states; Kansas and Oklahoma being large producers. Anhydrite, anhydrous calcium sulfate, is often associated with gypsum. This mineral is not suitable for the manufacture of plaster of Paris.

The usual plan of working the gypsum deposits is by mining, for deposits seldom lie near enough to the surface for quarrying. For the most part the mining methods are crude.

Manufacture of Plaster of Paris—The operation of manufacturing plaster of Paris from gypsum consists in first crushing and grinding the gypsum, then calcining the ground product, and finally pulverizing the calcined product, after which the retarders are added. In some plants the gypsum is merely crushed and calcined, the calcined rock then being ground very finely. Where the kettle process is employed, the pulverizing, however, is done before the calcining. Where the rotary cylinder process of calcining is used, the pulverizing is done after the calcining.

The gypsum is usually first crushed to such a size that it will pass a 2-in. screen. After the coarse crushers, the gypsum is further reduced by means of a double cone or pot crusher. These crack the gypsum to such a size that most of it will pass a ½-in. ring screen. From the pot crusher the gypsum passes to buhr-stones, rock-emery mills or in the newer plants, Raymond mills. These reduce the gypsum so that about 60 to 95 per cent of it will pass a No. 100 mesh sieve, the finer, the better the product. It is then ready to be fed to the kettles.

The Gypsum Kettle. The gypsum kettle, Figure 6, consists of a steel cylinder set in brick work. The bottom of the kettle is made of cast iron, and is convex in shape. It has a thickness of about ¾ in. at the edges and 4 ins. at the crown. This kettle bottom is a very important part of the apparatus, and is the part which seems to need repairing most often. The kettle itself is made of boiler plate, ⅜ to ⅝ in. thick. It is from 8 to 10 ft. in diameter and 6 to 8 ft. deep. A kettle of this size will hold from 7 to 12 tons of pulverized gypsum and produce from 5½ to 10 tons of plaster in one batch. It is provided with from two to four flues, 12 ins. in diameter, placed horizontally about 8 ins. above the crown of the kettle bottom. It is surrounded by brickwork, so the heated gas from the fire may rise around its sides and through the flues. The top is covered with sheet iron, and has a movable door and a vent to carry off the water. Two kettles are usually placed side by side and work in pairs.

It is necessary that the material be continually agitated. For this purpose the kettle is provided with a stirrer, which is actuated by a vertical pinion wheel and a line shaft. The stirrer itself consists of a cross arm which is curved to conform to the bottom of the kettle and provided with either paddles or a chain which drags along the kettle bottom. The stirrer is run at about 15 to 20 revolutions per minute, and is so arranged as to throw the material towards the center of the kettle. About 15 or 20 h.p. is required to operate the stirrer. If the gypsum is not stirred the charge will settle down and become hard. The bottom would be also melted out of the kettle.

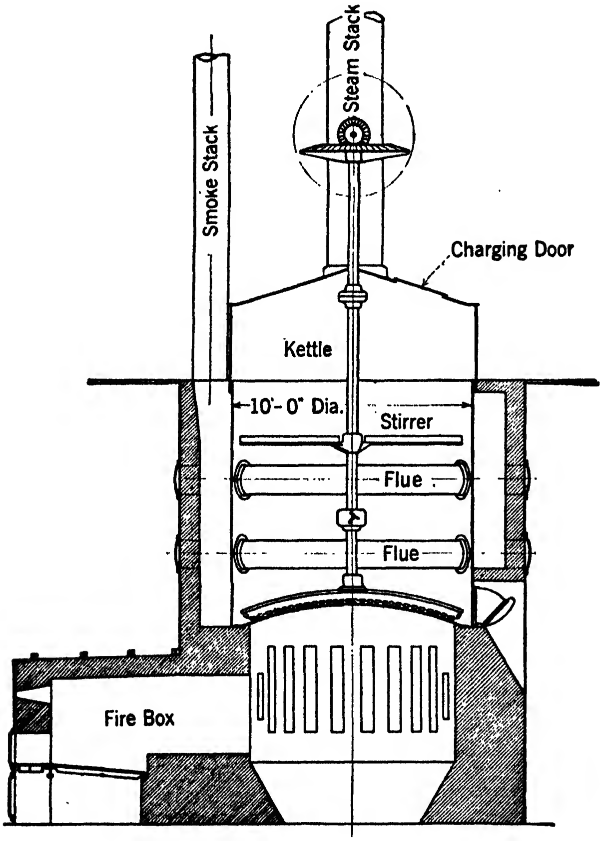

Fig. 6. Calcining Kettle for Plaster of Paris.

In starting a kettle, the heat is gradually applied, the crude material is fed in through the charging door and the stirrer put in motion. The material is added gradually until the kettle is full. As the temperature rises, the water begins to be driven off. The mechanically held water is first driven off at a temperature of 100° C., after which the contents remain fairly quiet until a temperature of 140° C. is reached, when the material begins to boil and the water of combination begins to be driven off. An expert calciner can tell by the way in which the charge boils when the process is finished. When the material has been calcined sufficiently it is run out into a pit by means of a small grate in the side of the kettle.

In burning pure gypsum the temperature rarely exceeds 170° C. Thermometers may here be used to advantage. In gypsite plants, however, a higher temperature is required, which may sometimes reach as high as 200° C. Here, owing to the complexity of the material, the proper temperature for calcining varies, and thermometers cannot be used.

It takes about 100 lbs. of coal to calcine a ton of plaster.

The gypsum kettles are arranged in pairs, with a pit to each pair of kettles, in order that the pit may be emptied from one charge while the other is being cooked. Sometimes the material is fully ground before calcining. Often, particularly in the older mills equipped with buhrstones, the grinding is done partly before and partly after calcining. In the latter event the calcined material is carried from the pit, by means of an elevator, to a bolting reel, where the coarse material, usually amounting to only a few per cent, is screened out, sent back to buhrstones and reground. From the bolting reel the material is conveyed to a storage bin. There are usually several of these in order to separate the runs of different days.

Rotary Calciners. The Cummer system of calcining consists in first partially crushing the material, so that it will pass a 1-in. ring screen. The gypsum crushed to this state is fed mechanically into a rotary drier or calciner. The material, in passing through the calciner, is heated to a temperature of from 175° to 200° C., the exact temperature depending upon the nature of the rock. From the drier the gypsum is carried into storage bins. They are built of vitrified brick or concrete, and are thoroughly ventilated so that they will not take fire or absorb the moisture given off by the gypsum. The calcining is completed in the bins, the moisture being driven off by the residual heat of the rock itself. After the gypsum has been dehydrated it is drawn out, crushed, ground, pulverized and bolted.

Adding the Retarder. The retarder is added to the plaster after it has been finely ground. Usually from 2 to 15 lbs. are required for every ton of plaster. The Broughton mixer is extensively used for this purpose. An ordinary wall plaster will also contain, in addition to a retarder, a certain per cent of finely picked hair or other fiber, in the proportion of about 1½ to 3 lbs. of hair to a ton of plaster. Wood fiber is sometimes added as a substitute for hair, and such use is growing.

Plaster is usually packed in jute sacks containing 100 lbs., or in paper bags containing 80 lbs. It is customary in the plaster trade, as in the cement trade, to charge for the jute sacks, and give a rebate on the return. Where the plaster is packed in paper bags, a charge is usually made for these.

Hard Plasters—Flooring plaster and hard-finished plaster are also gypsum products made by burning this mineral until all of its water crystallization is driven off. Flooring plasters are prepared by simply burning gypsum at a high temperature, while the hard-finish plasters are produced by a double burning with the intermediate use of some chemical. Flooring plasters are manufactured by burning pure gypsum, broken into lumps, in a vertical kiln. The kiln is heated by means of a grate, to one side of the kiln, upon which coal is fired. The hot products of combustion pass through, and so heat the gypsum in the kiln. The temperature reached is about 500° C. The time of burning is four hours.

These floor plasters give a very hard and durable surface, but they must be very carefully used to prevent cracking.

Of the hard plasters, Keene's is the best known, and was originally manufactured under an English patent. This, however, has long since expired. This cement is not only imported into this country, but is also manufactured to some extent here. It is made by burning a very pure gypsum at a red heat. The resulting anhydrous calcium sulfate is immersed in a bath of alum solution and dried, after which it is again burned at a high temperature, finely ground and placed upon the market. It is necessary to employ a very pure gypsum, as the slightest trace of iron would color the cement.

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