THE MANUFACTURE OF ACIDS AND ALKALIS

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Completely Revised and Rewritten under the Editorship of
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VOLUME VI

The Manufacture of Nitric Acid and Nitrates

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OF
Nitric Acid and Nitrates

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EDITOR'S PREFACE

THE first English edition of Lunge's *Sulphuric Acid and Alkali* appeared in 1879. Since that date the book has been revised and extended in subsequent editions until, with the companion volumes on *Coal Tar and Ammonia*, it extended to nine volumes, covering most of the heavy chemical industries of Britain. A supplementary volume on Sulphuric and Nitric Acids by Dr Lunge in 1917 marked the end of his long labours in this field, and he informed the publishers that he could no longer undertake the preparation of new editions. The mere compilation of the volumes which he wrote would be in itself a wonderful achievement, but Dr Lunge's place in the history of chemical industry is due still more to the fact that he played a leading part in the discoveries and improvements which built up the industries of which he wrote.

By a curious coincidence, the end of Dr Lunge's long literary labours came just as the processes which he originally described died out. The Hargreaves process has gone, in this country at least; the Leblanc process is dying, if not actually dead already; even the chamber process for sulphuric acid has now a competitor that threatens to become a rival.

The volumes written by Dr Lunge have escaped a common criticism of factory managers that books give only an outline of a manufacturing process; indeed the only criticism has been that Dr Lunge's books gave almost too much detail. It may, however, be realised how important is a detail relating to a matter involving a possible saving of only one-tenth of one per cent., when it is pointed out that this small economy in the manufacture of sulphuric acid would mean a saving of thousands of pounds, since the value of the sulphuric acid manufactured annually in Great Britain alone amounts to several million pounds.

Each new edition of this series has been an expansion and extension of that which preceded it, fuller treatment being accorded to subsidiary manufactures as they increased in commercial importance, until the name *Sulphuric Acid and Alkali* became a cover for what was practically an encyclopedia of the heavy chemical industries.

The last arrangement into volumes and parts was largely fortuitous, having arisen from uneven growth of knowledge and commercial development in different branches, and as this appeared to be a favourable opportunity for instituting a new arrangement, it was decided to sub-divide the work into sections more in accord with modern developments. The last few years have brought with them so many changes in the chemical industries that the revision required in most of the volumes will involve such drastic recasting that the new edition will be more a new book than a revised edition.

It is doubtful if any one man could take up Dr Lunge's task of describing adequately all the industries now dealt with in these volumes, and it is certain that few would care to attempt it. Each volume will therefore be on a special subject and dealt with by a separate author who is responsible for that volume, and is given a wide discretion in his treatment of the subject.

The editor trusts that these united efforts will produce a new edition worthy of the great tradition which Dr Lunge has established.

The editor will be pleased to consider for publication in this series any manuscripts or original work on this or allied subjects.

A. C. C.

LIVERPOOL, *March* 1923.

AUTHOR'S PREFACE

THE extended scope of the new and enlarged edition of Lunge's *Sulphuric Acid and Alkali*, of which this volume forms a part, has made it possible to present an account of the manufacture of nitric acid from Chili saltpetre much more fully than was attempted previously by Lunge.

Although I have taken advantage of the wealth of information provided by Lunge in previous editions, the present work is almost entirely new and embodies much of the experience gained in nitric acid and nitrate manufacture during the recent war years. Lunge's disconcerting breaks of continuity are avoided by collecting patents and references together at the ends of chapters, thus allowing the general reader freedom from a multitude of references but at the same time providing such extended information, and in a form more easily referred to, for those requiring it. Information kindly supplied from various sources in regard to the working of nitric acid plants has been given as received in order to retain for the readers direct contact with a number of different workers.

It is hoped that the method of treatment adopted will commend itself as being separately serviceable both for general reading and for reference purposes.

In compiling the present work I have made free use of published treaties and periodicals dealing with the subjects under consideration, and through the courtesy of the late Superintendent of H.M. Factory, Gretna (J. C. Burnham, Esq., C.S.I., C.B.E., B.Sc.), have had access to information available in the records of that factory.

I wish specially to thank W. L. Vellender, Esq., B.Sc., for very valuable help in the preparation of Chapters V. and VIII., Dr G. A. Welsh for the article on Acid Burns, Poisoning by Acid Gases and Medical Equipment, and N. V. S. Knibbs, Esq., B.Sc., A.I.C., for helpful criticism and for undertaking the tedious task of reading and correcting proofs.

My thanks are due and are hereby tendered to the Chilian Nitrate Committee for providing information forming the basis of Chapter I., and to the many firms and individuals who have so kindly placed information at my disposal.

Finally, I gratefully acknowledge the continued help given to me by my wife in the writing and arranging of the work.

ALLIN COTTRELL.

UNIVERSITY, EDINBURGH,
July 1923

CONTENTS

CHAPTER I

RAW MATERIALS FOR THE MANUFACTURE OF NITRIC ACID BY THE RETORT PROCESS

SULPHURIC ACID—*see* Vols. I., II., III., and IV. of this work

NITRATE OF SODA.

CHAPTER II

THE MANUFACTURE OF NITRIC ACID FROM CHILI SALTPETRE AND SULPHURIC ACID

CHAPTER III

NITRIC ACID MANUFACTURE—ANALYTICAL

CHAPTER IV

DENITRATION OF WASTE OR SPENT MIXED ACIDS

CHAPTER V

MIXED ACIDS

CHAPTER VI

PHYSICAL AND CHEMICAL PROPERTIES OF NITRIC ACID

CHAPTER VII

INDUSTRIALLY IMPORTANT NITRATES

CHAPTER VIII

AN ACID AND WATER BALANCE

NITRIC ACID AND NITRATES

CHAPTER I

RAW MATERIALS FOR THE MANUFACTURE OF NITRIC ACID BY THE RETORT PROCESS

NITRATE OF SODA.

Chili Deposits.

NATURAL deposits of nitrate of soda of vast extent are found in Chili. The usage of this material in agriculture and in chemical industries has led to intensive working of these deposits, and the industry which has developed in the production of nitrate of soda has assumed world-wide importance since their discovery in 1809.

It is estimated that the known deposits contain 240 million tons of available nitrate, and therefore it seems highly probable that the industry in Chili will remain of far-reaching importance for many years in spite of future developments in the fixation of atmospheric nitrogen.

It is certain, however, that if the industry is to continue successfully, the most diligent attention will have to be paid to the more economic extraction of the nitrate. Signs are not wanting that the Chilian nitrate producers are at last alive to the necessity of conducting careful research into the possibilities of more efficient methods of extraction.

Recently Professor F. G. Donnan has investigated the Chili nitrate industry for a group of English Companies, and the results of his study of existing inefficient practices, his recommendations for improvement and outlines for an elaborate general research programme are given in *Caliche*,[1] a publication devoted to the industry.

Uneconomic Extraction.—The following statement of an average nitrate officina's working,[2] shows in a striking way the serious extent of nitrate loss in the process at present in use.

	Unit.		
Weight of raw material—caliche .	1000 tons		
Nitrate content at 17 per cent. .	170 ,,		
Nitrate produced (50 per cent. yield) . . .		85 tons =	50 per cent.
Nitrate in refuse :—			
Bulk—ripio—at 3·4 per cent.		34 ,, =	20 ,,
Fines—borra		17 ,, =	10 ,,
Unaccounted losses		34 ,, =	20 ,,
		170 tons =	100 per cent.

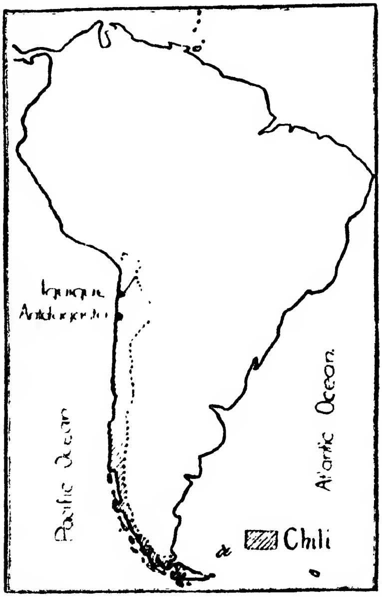

FIG. 1.—South America showing Chili.

Location. — The nitrate country proper is confined to a belt of Chili running north and south between latitudes 19° and 26° south, and lying mainly between 69° and 70° west longitude. The belt is approximately 420 miles long, but varies very much in width from about 3 miles in the north to 25 to 30 miles in the south. The deposits are not continuous, but are more or less massed at varying intervals throughout the nitrate belt.

NITRATE DISTRICTS.—For purposes of administration the various workings are grouped together into the following districts from north to south: (1) Tarapaca; (2) Tocopilla; (3) Antofagasta; (4) Aguas Blancas; (5) Taltal, the general

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[1] *Caliche*, 1921, 3, No. 9, 387-403; 1922, 3, No. 10, 457-70; 1922, 3, No. 11, 483-505.

[2] Hobsbaum and Grigioni, *J. Soc. Chem. Ind.*, 1917, 36, 57.

situation of which is indicated on the accompanying map (Fig. 2).

Character of Country.—Fig. 4 is a diagram showing a general cross section of the nitrate country from the sea coast to the Andes.

Fig. 3 shows a bird's-eye view of the same country. The whole district is sunburnt, bare, barren, and uninviting. The melting of the snows on the Andes feeds a number of rivers which flow in a westerly direction towards the sea. With one exception, however, the Rio Loa, these rivers eventually lose themselves in the plain before reaching the sea.

The region is practically rainless, but heavy moisture deposits in the form of dew are not infrequent. The prevailing wind is very regular, and blows from the west and south-west. The wind in approaching a hot land area becomes capable of holding more and more moisture. In passing over the coastal hills, however, the consequent rarefaction leads to formation of clouds and mists which are noticeable over the plain, but there is no notable rainfall until the Andes are reached.

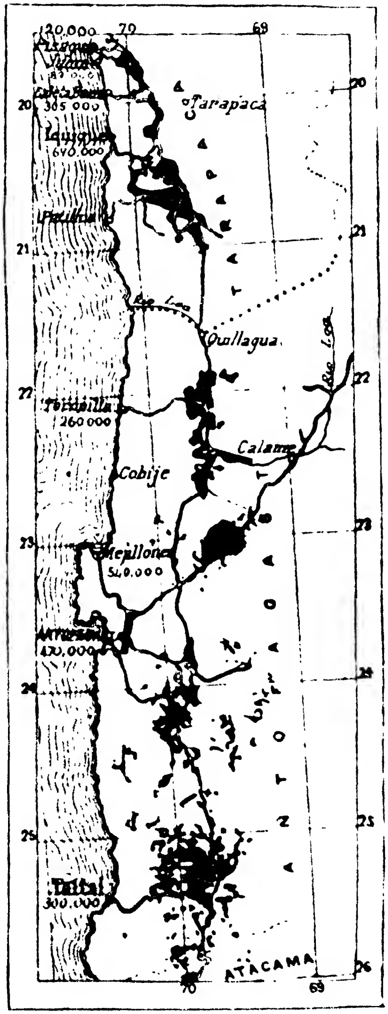

Fig. 2.—Nitrate Districts (Bertrand).[1]

The coastal hills form a barrier between the plain and the sea, and natural depressions on the landward side of these hills—which would be so many

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[1] *Chim. et Industrie*, 1920.

lakes if evaporation and infiltration did not much exceed the corresponding condensation—contain the accumulated saline residue of the evaporation of centuries.

TEMPERATURE.—As is to be expected from the elevated position of the nitrate areas the days are very hot, and the nights cold. The temperature varies between 77° and 96° F. (25° and 35° C.) during the day, and 40° and 46° F. (4° and 8° C.) during the night.

Theories of Formation.—Many theories have been put forward to account for the presence of the accumulations of nitrate of soda and other salts in these areas. One of these is that the beds were originally guano deposits similar to the existing guano beds of Peru, but the absence from the nitrate deposits of phosphates, which are always present in guano, is a serious objection to this theory. Another suggests that they are the remains of stores of marine vegetation which existed in a volcanically trapped inland sea, since dried up. This theory does not explain the absence of bromides which would be expected from the decay of algal matter. A more recent theory postulates intense electrical activity in the air during past periods, with resulting production of oxides of nitrogen. The nitric acid produced by interaction of these gases with torrential rainfalls, acted on the mineral constituents of the soil, producing nitrate which infiltered in solution. Subsequent capillary attraction brought the solution to the surface, and this resulted in deposition of the contained salts.

Ports.—The ports actively engaged in the exportation of nitrate are connected with the nitrate fields by systems of railway. Unfortunately the railways are of varying gauge, and this hampers freedom of transport throughout the area. The yearly export capacities in tons of nitrate of these ports are indicated on Fig. 2.

The Nitrate Beds (Caliche).—The actual deposit of nitrate material known as "caliche" lies in layers ranging from a few inches to 3 or even 6 ft. thick. The caliche lies under an overburden of soft and hard layers of "chuca" and "costra," containing variable quantities of silica and chlorides, sulphates, carbonates, etc., chiefly of sodium, potassium, and calcium. This overburden varies from 1½ ft. to as much as 20 ft. in

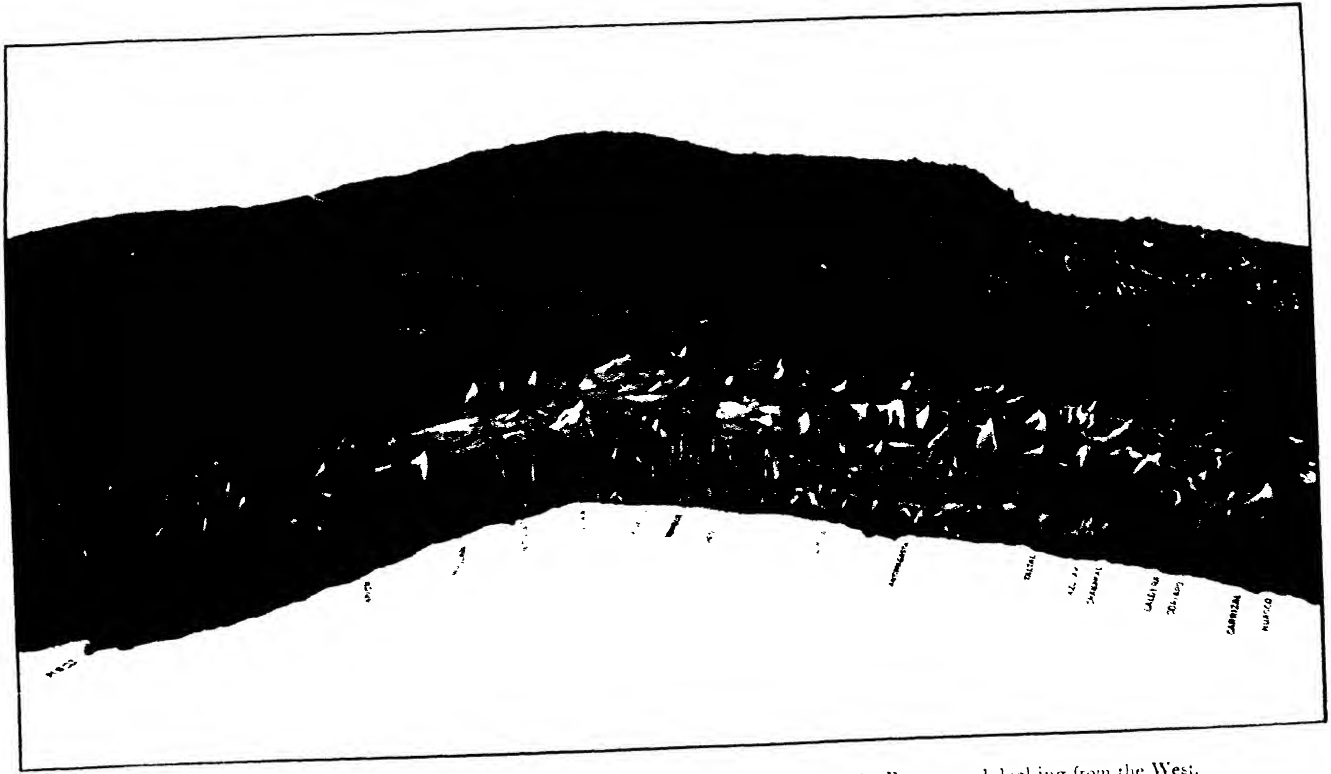

FIG. 3.—Part of the South American Continent, with Chilian Nitrate Fields in the Foreground, looking from the West.

[Face page 4

thickness. Between the caliche and the underlying volcanic rocky skeleton of the country lie the "conjelo" composed of soluble salts (excluding nitrate) and the "coba," consisting of loose sand and gravel.

COMPOSITION.—Caliche varies in colour from white to black through many shades of brown. It is an extremely complex and variable conglomerate, with stony and clayey insoluble matters firmly cemented by soluble salts. The proportion of insolubles ranges from 0 to 60 per cent. in different specimens. The soluble salts contained in caliche are extremely numerous, yet they do not all necessarily exist together. The following table,[1] gives the approximate composition of various caliches at present being worked.

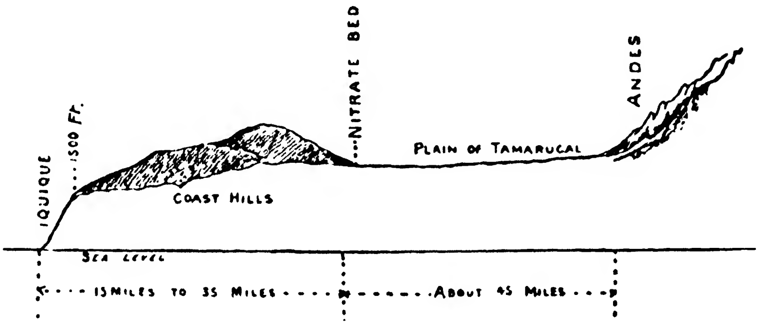

FIG. 4.—General East and West Section of the Nitrate District of Chili—Vertical Scale exaggerated.

	Per cent.		Per cent.
$NaNO_3$	14 to 30	Borates of sodium and calcium	1 to 2
KNO_3	2 „ 6	$NaIO_3$	0·02 „ 0·2
NaCl	8 „ 25		
Insolubles	25 „ 50	Perchlorates	Traces
$CaSO_4$	2 „ 6	Chromates	
Na_2SO_4 $MgSO_4$	2 „ 6	Sulphonitrates	
		Vanadates	

The analyses shown on next page are from Hobsbaum and Grigioni.[2]

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[1] Donnan, *Chem. Age* (London), 1919, 1, 634-35.

[2] *J. Soc. Chem. Ind.*, 36, 2, 53.

Analyses of Caliches.

Per cent.	High Grade.				Low Grade.			
	1.	2.	3.	4.	1.	2.	3.	4.
Moisture . . .	1·107	2·003	1·121	2·764	1·061	1·892	2·173	1·951
Potassium nitrate .	...	...	...	...	0·958	...	...	...
Sodium nitrate .	52·960	48·700	50·250	33·687	13·270	12·4	14·034	13·160
,, chloride .	23·4	17·3	30·2	25·7	29·3	13·9	17·8	9·1
,, iodate .	0·074	0·151	0·026	0·014	0·059	0·062	0·010	0·152
,, sulphate .	2·976	6·958	1·226	...	8·220	0·075	...	6·246
Magnesium sulphate	1·166	2·441	0·156	...	0·885	7·041	...	3·087
Calcium sulphate .	2·585	2·177	3·110	3·230	4·026	3·618	5·456	3·346
,, nitrate .	...	...	...	...	...	...	3·935	...
Insoluble . .	15·677	20·213	13·9	34·597	42·213	51·934	56·543	62·938
	99·945	99·943	99·989	99·992	99·992	99·922	99·951	99·980

The average of a large number of samples of caliche from various districts gave the following percentage composition.[1]

	Per Cent.
$NaNO_3$	20·0
KNO_3	trace
$NaCl$	20·13
Na_2SO_4	2·80
$CaSO_4$	6·37
$MgSO_4$	4·05
Insolubles	45·50
$NaIO_3$	0·15
Undetermined	1·00

PHYSICAL STRUCTURE.—The physical structure of caliche is very variable, and this has an important bearing on its lixiviation. It is most commonly a breccia-like mass with stony nodules, and is of medium hardness. Some samples are spongy, some clayey, while others are very hard. Certain hygroscopic caliches owe their character to their calcium nitrate content. The hardness of caliche is important from the point of view of crushing, and is to a large extent dependent upon the nature of the insolubles.

DENSITY.—The real density of caliche varies from 2·1 to 2·3.

Prospecting for Nitrates. — Prospecting is done by

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[1] F. C. Harold, private communication.

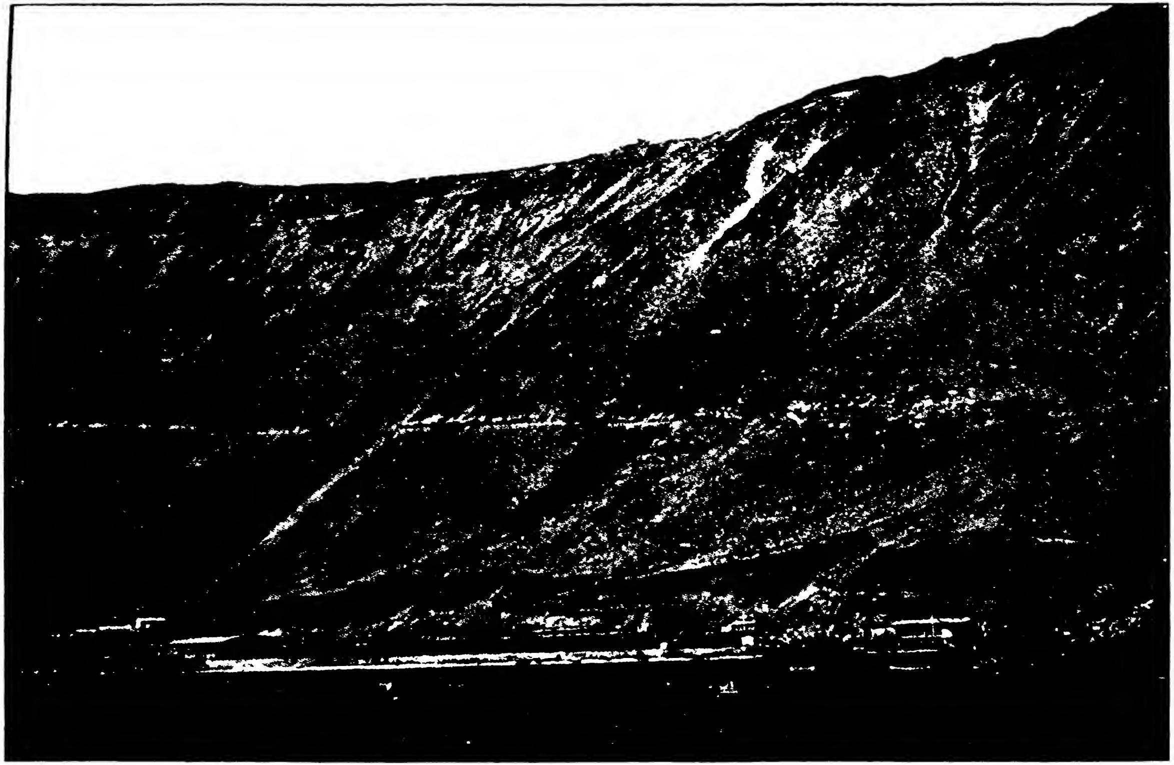

FIG. 5.—General View of Junin.

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systematically boring test holes at intervals of about 120 yards over the area to be covered. The workers bore holes with

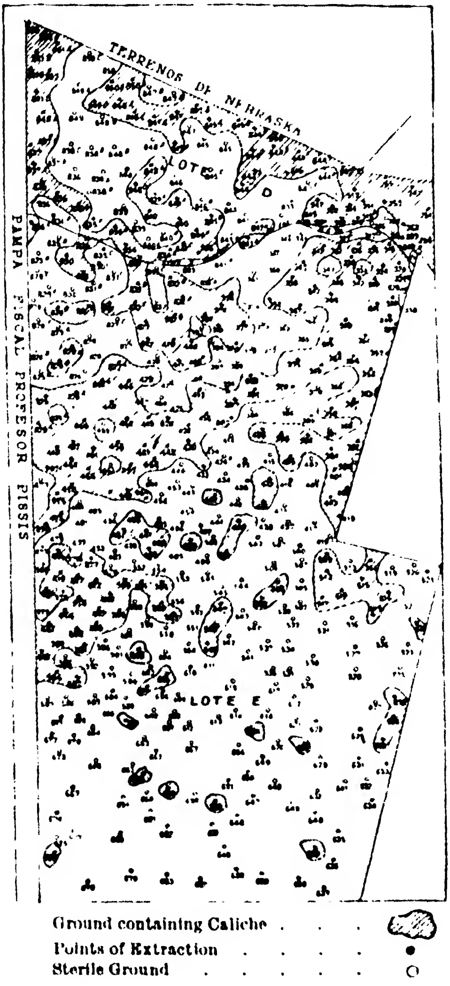

FIG. 6.—Portion of Prospection Plan (Bertrand).[1]

steel bars, and remove samples with long scoops. Only occasionally is it necessary to use explosives in sampling.

The accompanying plan (Fig. 6) shows a portion of a

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[1] *Chim. et Industrie*, 1920.

Typical Extract of the Prospecting Sheet at Santa Laura. Lot D.

Number of Prospecting Hole.	Thickness of Superposed Layers, Metres.		Thickness of Caliche, Metres.	Thickness of Substrata, Metres.	Total Thickness, Metres.	Percentage Contents.					Product (Thickness multiplied by Percentage Contents.)
						Nitrates.		Chlorides.	Iodine.	Sulphates.	
	Sterile.	Crust.				Crust.	Caliche.				
239	0·20	...	1·20	0·85	2·25	...	17·3	...	...	...	20·760
240	0·25	...	1·25	1·50	3·00	...	16·5	23·8	0·0291	9·56	20·625
246	0·80	...	1·20	0·75	2·75	...	12·8	...	...	...	15·360
247	0·75	...	0·75	0·95	2·60	...	18·8	...	...	...	14·100
248	0·40	...	0·90	1·27	2·57	...	15·0	...	...	...	13·500
249	0·16	...	0·67	2·12	3·95	...	10·2	...	...	...	6·834
250	0·15	...	1·55	1·50	3·20	...	11·5	...	...	...	17·825
251	0·10	..	0·90	1·67	3·67	...	17·2	...	...	...	15·480
252	0·90	...	0·75	2·30	4·05	...	16·7	...	...	...	12·525
253	2·30	0·70	...	0·38	3·38	7·4	...	...	...	..	5·180
254	0·22	2·08	...	2·05	4·35	11·4	...	...	...	...	29·952

NOTE.—1 m. = 3·28 ft.   1 sq. m. = 10·76 sq. ft.

typical nitrate area. It is part of one of the plans published by the Chilian Government indicating the prospecting which has been done on ground granted for auction.

The official publication accompanying such a plan shows, for each test hole, the thickness of the covering layers, of the caliche, and of the under layers, also the content of nitrate of soda, chlorides, iodine, and sulphates (see Table on p. 8).

Further information is shown below.

Typical Economic Sheet of a Prospecting Nitrate Lot.

SANTA LAURA.

	Sq. Metres.
Area of the caliche deposit	1,063,950
Area sterile	305,426
Total area	1,369,376
	Number.
Holes indicating the presence of caliche	144
Holes sterile	40
Total number of prospecting holes	184
	Metres.
Average thickness of caliche	0·980
Average thickness of sterile ground	0·705
Total thickness	1·685
	Per Cent.
Average nitrates in caliche	16·39
Average chlorides in caliche	20·00
Average iodine in caliche	0·0665
Average sulphates in caliche	7·36
Theoretical volume of the caliche, c.m.	1,042,665·9
Quantity of caliche per c.m., tons (Average density, 2·231)	2·231
	Tons.
Total weight of caliche	2,326,187·6
Less 23 per cent. waste	535,023·1
Weight of working caliche	1,791,164·5
Weight of recuperable nitrate	293,571·85

Production of Nitrate of Soda. — The nitrate-bearing material, caliche, has to be quarried, and the sodium nitrate separated from the insolubles and the other soluble salts.

Historical.—The separation of nitrate of soda from the natural deposits of South America dates back to 1809. An impetus was given to its production about 1830, when its use as a fertiliser was recognised in Europe.

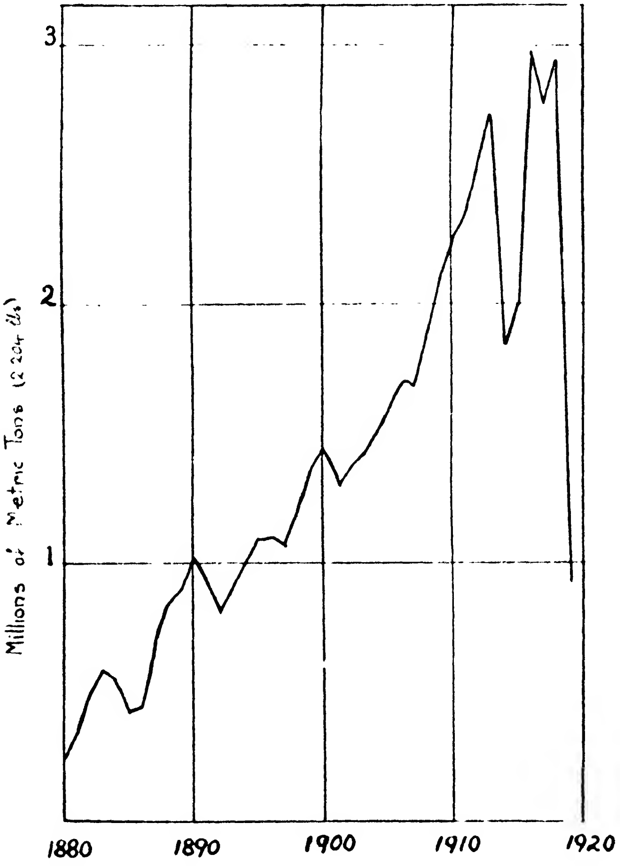

Fig. 7.—Exports of Chilian Nitrate.

During the primitive period of production caliches containing less than 50 per cent. of nitrate of soda were seldom worked—often the content was 60 to 80 per cent. This rich caliche was lixiviated in pans over open fires. The boiling liquor was removed by ladles to settling tanks, where the insolubles and suspended chloride were deposited. As soon as the liquid cleared it was ladled to other pans where it was

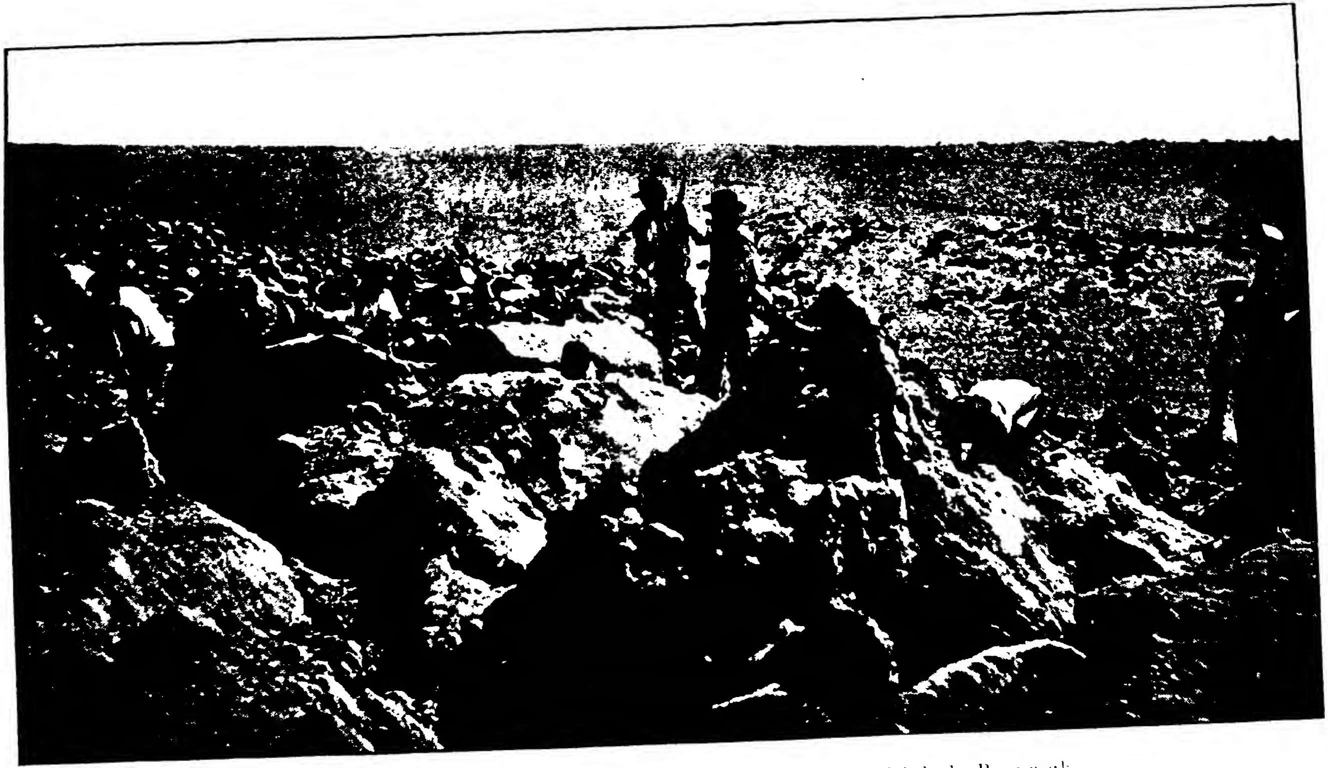

FIG. 8.—Opening up Trench after Blasting: showing Extraction of Caliche by Piece-work.

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allowed to crystallise. Only occasionally were the residues (containing 15 to 25 per cent. of nitrate) submitted to a second lixiviation. Prior to 1856 about 200,000 tons of nitrate were won in this manner.

From 1856 improvements in practice were gradually introduced, although the method of nitrate extraction remained fundamentally the same. Open fires were done away with, and steam (generated at 40 to 60 lb. per square inch) was injected in the boiling tank through a perforated pipe placed on the bottom. Larger tanks were also introduced. Later, closed steam coils were used to provide heat in the boiling tanks without bringing about dilution of the liquor. From 1856 to 1876 some 3 to 4 million tons of nitrate were produced from caliches containing at least 50 per cent. of nitrate.

SHANKS PROCESS.—From 1876 dates the introduction, by Mr J. T. Humberstone, of the Shanks process of methodical lixiviation, and this process has continued without material alteration of method up to the present time. Since 1876 hundreds of large and costly installations have been constructed, and about 55 million tons of nitrate have been extracted by this method. In this period the annual production of nitrate of soda has risen from 300,000 tons to 3 million tons (Fig. 7).

PRESENT METHODS—*Mining.*—The loose top covering of the caliche is removed and the caliche broken up by blasting. Bore holes are driven through the caliche into the coba layer underneath. Here a charge of slowly exploding gunpowder, made on the works, is placed. On firing, much of the loose covering layer is blown away, and the bed of caliche is broken up. An explosion with a large rupturing power is desirable so that as big an area as possible is made workable. Workmen now clear the loose covering material, and the caliche is then further broken up by use of dynamite cartridges and hand tools. The caliche is then hand picked and loaded into strongly built mule carts, which carry it either to the works or to the railway loading stations where it is loaded into tip-up wagons en route for the works.

Note.—The workmen are able to gain a fairly accurate estimate of the nitrate content—to within 2 per cent. of the material handled—by crushing a little, throwing it on to glowing tinder and noting its behaviour.

Crushing. — At the works the caliche is delivered to a receiving hopper placed at a high level. From here it feeds to jaw crushers where it is broken into lumps measuring up to 4 in. Usually the material from the crushers is not screened, but recently steps have been taken to screen the material both before and after crushing, and so ease the subsequent lixiviation process.

Lixiviation.—The crushed caliche is raised to the top of the boiling tanks by elevator or conveyer, and is supplied to the tanks through portholes in the roofs as desired. The boiling tanks vary in size, shape, and points of construction from works to works, but usually they are built of heavy sheet iron, and are about 25 to 40 ft. long, by 7 ft. wide, by 9 ft. deep, with a maximum caliche capacity of 80 tons. They are covered, and the lids have inlet ports for admission of caliche. The tanks are raised some 10 to 12 ft. from the ground, have false bottoms composed of perforated plate placed about 8 in. from the true bottom, and are fitted with three or four large doors in the bottom, opening outwards. These doors serve for the removal of insoluble residue after boiling. Low pressure steam circulates through closed iron coils running along the sides

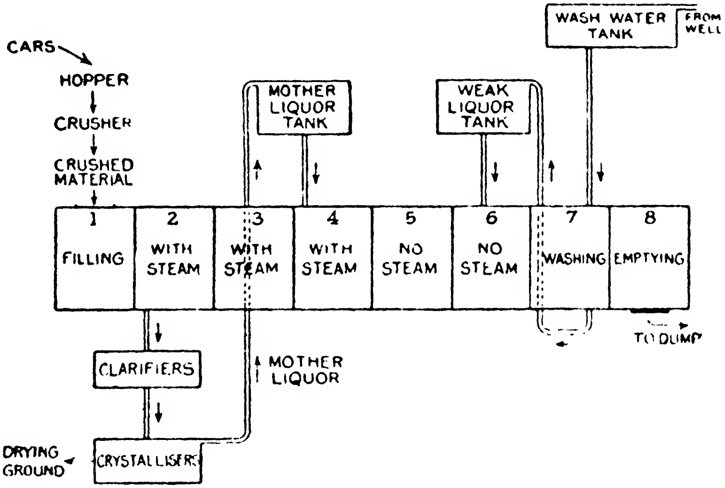

FIG. 9.—Flow of Material in Shanks Process (Donnan).[1]

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[1] *Chem. Age* (London), 1919, 1, 635.

and ends of the tanks and provides the necessary heating. The tanks are interconnected by hand pumps or siphons and have run off pipes for the liquors.

A 100,000 tons-per-year plant needs approximately fifty such boiling tanks.

The lixiviation is carried on by the counter-current principle, and usually takes place in batches of eight tanks which constitute a cyclic system.

The diagram in Fig. 9 shows the flow of material through a nitrate plant. In this drawing, boiling tank 8 is represented as being emptied of spent material after extraction of as much nitrate as possible. Tank 7 contains material not quite spent, and it is filled up with fresh water obtained either from deep wells, or from a river. This almost spent material enriches the wash water and provides a weak liquor which is pumped to a weak liquor store tank. Tank 6 contains rather richer material, and it receives a washing with weak liquor supplied from the store tank. Further enriched with soluble salts, the liquor in tank 6 is pumped over into tank 5, which contains material one step further removed from the spent stage. From tank 5 the liquor is passed forward to tank 4, where steam is turned on and the liquid brought to boil in contact with material still richer in nitrate. The liquor is then passed forward to tanks 3 and 2 in turn, where boiling also takes place. The liquor passing into tank 2 comes in contact with newly charged caliche, and soon becomes as

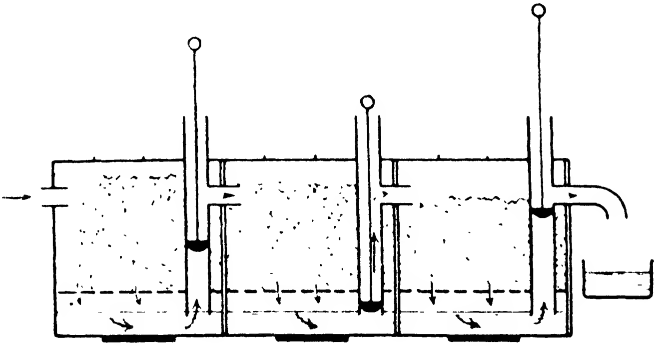

FIG. 10.—Diagram showing Means of Circulation of Liquor, False Bottom, Pump, and Side Pump, Discharge Hole, and Charging Portholes (Donnan).

highly charged with soluble salts as is possible at the temperature used, about 120° C. At this stage it contains approximately 50 per cent. of nitrate of soda, and it is run off into clarification tanks.

The end of the lixiviation process is usually determined by noting the density of the liquor. This is, however, only a rough guide, as the density is affected by the presence of varying quantities of substances other than nitrate of soda in solution, and by fine particles of clay and other insolubles in suspension.

When the boiling liquor is sufficiently concentrated, it is slowly run off from a point just above half way up the tank. The level of the liquor is maintained by feeding fresh liquor forward from tank 3 which is fed from tank 2, and so on. The concentrated liquor (known as "caldo") is kept boiling and is run off slowly until its strength falls below that necessary for crystallisation.

The above movement of liquor through the tank cycle is continued until the density of the liquor in tank 2 shows that the necessary concentration has not been reached. At this point, tank 7 which lately had a cold water wash, becomes the last tank of the cycle and is emptied. Tank 1 now is included in the liquor series, and so the cycle is continued. The complete washing of one batch of material takes from twelve to twenty-four hours. Owing to the inadequacy of the density test for saturation, it is common to have either incomplete washing with excess of nitrate lost in the residue, or unnecessary washing with additional heat consumption.

The exhausted material left in the boiling tanks consists of a coarse material ("ripio") above the false bottom, and a small quantity of fine soft clay ("borra") which has collected under the false bottom. This exhausted material is first poled out of the discharge doors by workmen standing on the roof of the tank, and then a gang of workmen get inside the tank and shovel out the remainder. The residue is caught in rail bogies stationed under the tanks and is conveyed to the waste dump.

Normal good working results in an extraction of 50 to 60 per cent. of the nitrate content of the caliche, leaving a residue containing 5 to 8 per cent. of nitrate. As already indicated,

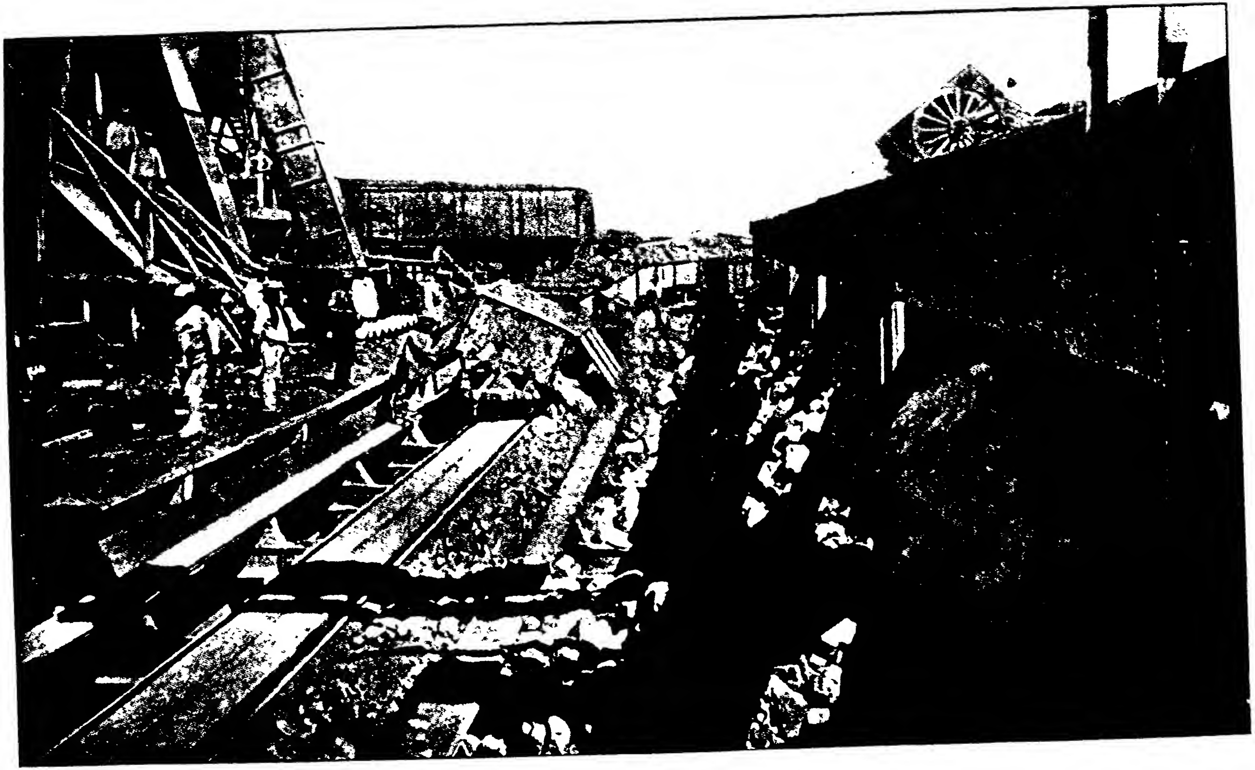

FIG. 11.—Top of Caliche Hopper; Carts tipping Caliche.

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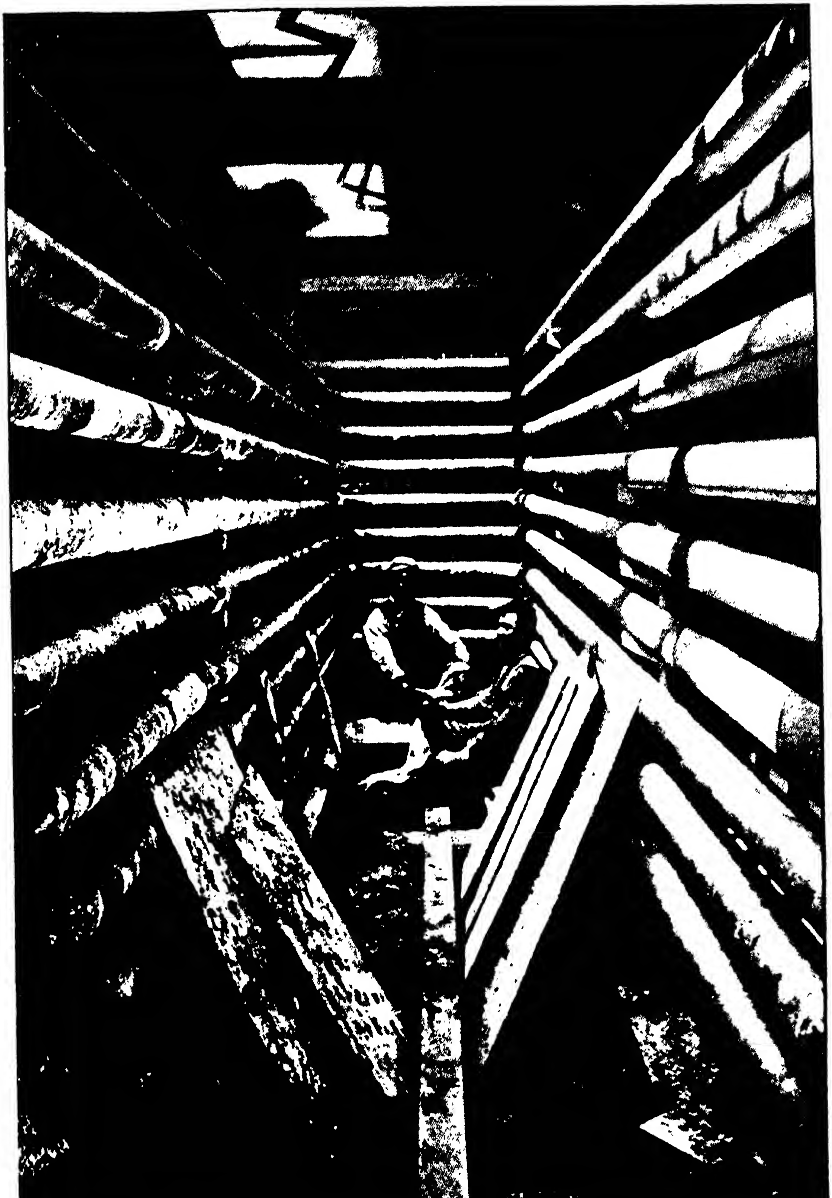

FIG. 12.—Interior of a Boiling Tank.

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old refuse heaps may contain up to 20 per cent. nitrate, and thus it is seen that the vast accumulations of refuse at the works are potential sources of nitrate of soda.

Clarification and Decantation.—The clarification vessels are rectangular tanks of sheet iron 12 to 18 ft. long by 6 to 10 ft. wide, by 3 to 7 ft. deep, and have sloping bottoms. They are large enough to take the saturated liquor from a twenty-four hours' operation. To facilitate settling, materials which flocculate the suspended matter are added. Amongst those employed are flour, animal glue, lime, sodium carbonate, and guano. The clarified liquor is run off to crystallisation tanks.

Crystallisation.—The crystallisation tanks are of heavy sheet iron 12 to 20 feet long by 10 to 15 ft. wide by 3 to 3½ ft. deep. The bottom of the tank slopes to one side to facilitate draining, and is provided with two to four plugged outlets. The total capacity of the crystallising tanks is usually about twice that of the boiling tanks. The liquor is allowed to stand to crystallise for six to twelve days at atmospheric temperature.

Theoretically the mother-liquor should still contain nitrate of soda to the extent of 400 grams per litre at a temperature of 10° C., and there should not be any precipitation of sodium chloride, but owing to the great amount of evaporation (3 to 4 per cent. of the volume), the saturation limit of sodium chloride may be reached and the salt deposited.

The nitrate of soda so obtained is of 95 per cent. purity and contains about 2 per cent. of sodium chloride. For the chemical industries a refined nitrate is produced of 96 per cent. nitrate content, and not more than 1 per cent. of sodium chloride. This refined nitrate is obtained by washing the 95 per cent. material with a small quantity of fresh water or with a solution of pure nitrate of soda. On some plants, however, this refined nitrate is obtained direct by longer settling and deposition of sodium chloride in the clarification tanks.

After crystallisation is complete, the plugs in the crystallising tanks are removed and the mother-liquor allowed to drain into canals which lead via straining pans to a sump from where it is pumped up to the mother-liquor tank, and introduced as required into the lixiviation cycle at the tank containing liquor of about the same concentration.

Drying.—The crystals of nitrate are shovelled to the high ends of the tanks or out on to draining boards and allowed to drain for one or two days, when they are transferred by trolleys to the drying grounds, which are either earth, wood, or concrete floored.

The moisture content at this stage is about 12 per cent., but in the dry atmosphere it is soon reduced approximately to 2 to 3 per cent. Drainage entails a slight loss of nitrate.

SHIPMENT.—When the nitrate is sufficiently dry it is filled into bags holding 2 quintals (200 lb. approx.) net, and railed to the nearest port for shipment. At the port, the nitrate is transferred to lighters which carry it to vessels anchored off shore.

RECENT DEVELOPMENTS.—Several nitrate companies have already taken steps to modify the original Shanks process of nitrate extraction, but no new system has yet proved so strikingly successful as to be generally accepted by the conservative nitrate producers.

Butters Process.—The Butters process was introduced in 1915 at the Agua Santa property in Tarapaca, and is claimed to have proved more economical and efficient than the original process. The Butters system, as worked, is only an adjunct to the Shanks process, and consists in screening the caliche and leaching the fines separately from the lump material. The lump material is put through the normal process whilst the fines, along with the fines' residues from the Shanks process, are subjected to thorough disintegration in a ball mill in presence of hot weak nitrate liquor. The slurry thus produced is heated by steam coils and then filtered in the Butters vacuum filter. The Butters filter consists of big double leaves of canvas filter cloth stretched over a framework of iron tubing, many units being connected together by common headers. The filter leaves are immersed in the slurry to be filtered. The filter cakes are given two washes, the final one being with a saturated solution of sodium chloride, and are finally discharged with a nitrate content of about 0·25 per cent. By this combined treatment it is claimed that it has been possible to increase the efficiency of working a 15 per cent. caliche from 7 to 10 per cent., and to lower the operating cost about 20 per cent.

Gibbs Process.—During 1912 to 1914 Messrs Gibbs & Co.

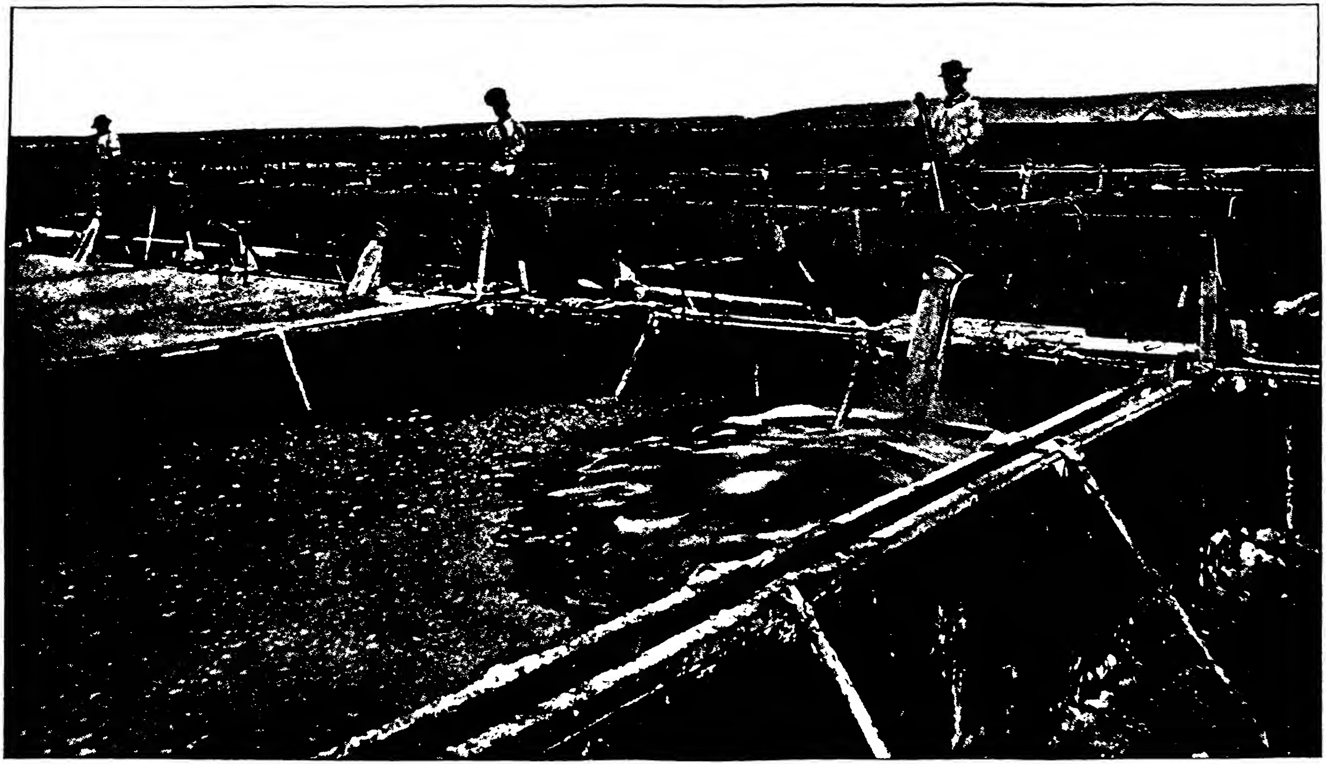

FIG. 13.—Crystallising Pans Full, Filling, and Empty.

[*Face page* 16.

of Valparaiso worked out an improved process successfully adapted to the working of even poor slimy caliches, and the first Gibbs plant was erected for the Fortuna Nitrate Company for their officina Celia, Antofagasta, in 1917.

The Gibbs treatment is based largely on successful metallurgical practice in the winning of gold from ores by the cyanide process, and starts out with the object of first removing from the caliche the small particles of clayey material which are slime formers, and which do so much to prevent intimate contact of liquor and soluble material in the normal boiling process.

Caliche is crushed to 2 or 3 in., and is then fed into a tube mill, together with nitrate solution at about 50° C. The mill works without balls or pebbles, and is designed not to crush but merely to break down the conglomerate to its ultimate constituent particles.

The pulp is passed continuously from the mill to a series of classifiers, such as are used in metallurgical practice, where the raw material is lixiviated on the counter-current principle. The liquid and slow settling solids (slime producers) overflow at the closed lower end to suitably placed thickening tanks (where clear liquor is separated from thick liquor), while the quick settling solids are conveyed along the bottom by mechanically operated rakes, and after emerging above the liquid line are discharged to the next classifier in sequence.

From the last classifier, the insolubles are discharged with not more than 0·25 per cent. nitrate. They consist of loose sand, gravel, and stones, and are easily washed and drained.

The thick liquor from the thickening tank, which is a saturated solution of nitrate, chloride, etc., along with the fine sands and slimes, is subjected to filtration in an Oliver continuous vacuum filter, which has a revolving drum with about one-third of its circumference at a time dipping under the liquid to be filtered. The drum is divided into compartments, over which a filter medium is stretched, and each compartment is connected by two pipes to an automatic valve which controls the application of vacuum for forming and washing the cake, and the admission of compressed air for discharge of the cake, and for cleansing the filter medium. Provision is made for washing the cake, and a scraper ensures its complete removal after loosening by compressed air. An agitator inside the filter tank prevents settling and ensures a uniform cake.

In operation, suction is applied to the sections of the drum on which the cake is being formed and to those which are being washed. The vacuum is then broken to permit free discharge of the cake.

The clear liquor separated in the thickening tank is circulated by pumps over the material in the classifiers.

Fig. 14 gives a diagrammatic representation of the scheme.

The process is designed to give a filtered liquor containing about 450 grams of nitrate, 200 grams of chloride, and 50 to 60 grams of other solubles per litre, although by working at higher temperatures a more concentrated solution could be obtained.

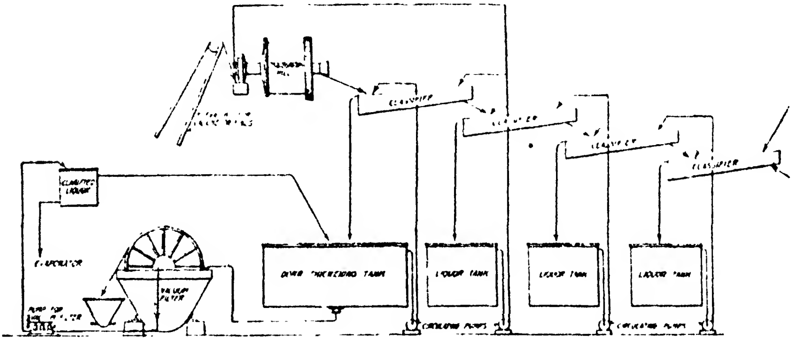

FIG. 14.—Lixiviation Plant and Cycle of Operations used in Nitrate Leaching. (Gibbs Process).[1]

A 95 per cent. extraction is claimed, and if this is substantiated in large scale working, the process should go a long way towards solving the economic extraction of nitrate from caliche.

The filtered liquor has to be concentrated, and this is done in Kestner double effect evaporators of the salting type. Evaporation is carried out in two stages, the first aiming at the almost complete separation and recovery of sodium chloride, while the second recovers the nitrate of soda as crystals. The first stage is carried out in the first effect at 124° C. under atmospheric pressure. At this temperature practically all the

[1] *Eng. and Min. J.*, 1st June 1918.

FIG. 15.—Emptying Crystallising Pans into Cars.

[Face page 18.

chloride is thrown out of solution, and provision is made for transferring the desalted liquor to the nitrate crystalliser, which is a vacuum effect at 80° C. without calandrias. Here, in the second stage, by cooling and self-evaporation under vacuum, the nitrate crystallises immediately and is removed from the cooled bottom by a screw, cooled, and dried in hydro-extractors.

The mother-liquor from the hydro-extractors is periodically tested for calcium and magnesium salts, which are converted into sodium salts as necessary before being returned to the system. The iodine will be dealt with in the usual way.

The advantages claimed by the Gibbs process are:—

1. Cheapness of installation.
2. Ability to treat cheaply and effectively low-grade caliches with an overall extraction efficiency of 90 per cent.
3. Ease of control of process.
4. Direct crystallisation of nitrate, ensuring ability to trace losses and remove their causes at once.
5. Greater control over the working of the nitrate deposits which, owing to the necessity of hand selection, can not be mined economically by mechanical means.

The author is indebted to Mr F. W. Bishop lately Secretary for the Fortuna Nitrate Company, for the following statement: "Prior to the sale (of the Fortuna Nitrate property in 1920), the Gibbs process was giving satisfaction and demonstrated that low ley material could be treated by it at a satisfactory cost; moreover, much lower quality material could be dealt with than under the old system of working."

PATENTS.—Of the numerous patents (300 or so) which have been taken out in Chili relating to the nitrate industry, about 34 per cent. deal with the lixiviation stage. Many of these propose to accelerate the process by mechanical methods such as agitation, etc. Other proposals are: (1) Preliminary classification of raw material; (2) to dispense with heating; (3) to render the operation continuous; (4) to operate in closed tanks under pressure or under partial vacuum; (5) to lixiviate at the nitrate beds and transport liquor to works situated at the ports.

About 27 per cent. refer to points of practice in evaporation and crystallisation, 10 per cent. to the economy of heat, 10 per cent. to the treatment of pulverised caliche and recovery of nitrate from residues, and 19 per cent. to the recovery of by-products.

RESERVES OF CALICHE. — According to reports by the Chilian Nitrate Committee, the nitrate of soda in the ground already examined is estimated at 245,300,000 tons, and this ground is less than 3 per cent. of the total nitrate area.

WATER. — At the present time the water consumption is from 20 to 50 galls. per quintal (101·4 lb.) of nitrate, meaning a total annual requirement of 2000 to 3000 million galls.

The rivers formed by the melting of the snows on the Andes provide this water, though there are also available large reserves of underground water in the nitrate regions. The underground water is highly charged with mineral salts, containing up to 1 per cent. of sodium chloride and appreciable quantities of carbonates and sulphates of calcium and magnesium. This water is therefore unsuitable for use in steam production without previous purification.

FUEL.—The present (1916) annual consumption of fuel, including that used on railways of the nitrate areas, amounts to over 300,000 tons of coal and 800,000 tons of oil. As this has to be imported from Europe and the U.S.A., the question of its economic consumption is of vital importance. Of the fuel used on the nitrate works 20 per cent. is required for power and 80 per cent. for heating. With present methods of heating the efficiency of fuel consumption is only about 35 per cent.

POWER.—With a caliche of 18 per cent. nitrate content the power usage is approx. 1 kw. year per 1000 tons of nitrate, the distribution being as follows:—

Crushing and transportation . . .	70 per cent.
Circulation of liquids	15 ,,
Workshops	5 ,,
Light	10 ,,

The tendency now is to do away with separate power plants for each works, and to obtain power from a few central power stations which serve the whole nitrate region.

PROBLEMS OF THE INDUSTRY.—Before maximum efficiency of production and minimum cost of nitrate can be attained, many problems will have to be solved. These include problems of surveying, mining, transportation from mines to works, heating, lixiviation, evaporation, crystallisation, transport from the works to the ships, the further utilisation of mechanical appliances in many directions, administration, etc., etc.

During 1918 the Chilian Government and the nitrate producers joined forces in an attempt to solve many of these important problems, and towards the close of the year a technical institute for nitrate research was established in Chili. A scientific society has also been formed by a number of Chilian and English companies.

The various national interests in the Chilian nitrate industry are approximately :—[1]

Chilian	36 per cent.
British	34 „
German	18 „
Yugo-Slav	10 „
American	2 „

Costs.—Detailed analytical costs for nitrate production have not hitherto been obtainable, but close observation, with all available facilities, permits approximations to be made in regard to the relative cost items.

Such approximations are given below :—

A. *Works Operation Costs.*

1. Labour .	from	42	to	25	per cent.
2. Fuel . .	„	50	„	60	„
3. Water .	„	5	„	10	„
4. Materials .	„	3	„	5	„
		100		100	„

These figures show the economic importance of fuel consumption and labour factors.

B. *General Production Costs.*

		Pre-war.			June 1918.				Per cent.		
1. Extraction of caliche	from	6d.	to	14d.	27d.	per Span. quintal	=	22	to	35
2. Transportation	„	3d.	„	7d.	10d.	„ „	=	10	„	15
3. Works operation	„	17d.	„	17d.	32d.	„ „	=	60	„	45
4. General expenses	„	2d.	„	2d.	3d.	„ „	=	8	„	5
Total	„	28d.	to	40d.	72d.			100	to	100

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[1] H.M. Consul at Antofagasta, 1920.

C. *Summary of Cost Price of Nitrate on Board Ship.*

	Pre-war.		1918.	
	S.	D.	S.	D.
1. Interest and Sinking Fund	0	9	0	9
2. Cost on drying floors	2	8	6	0
3. Transportation to ship	0	11	1	0
4. Export duty	2	4	2	8
	6	8	10	5

Per Spanish quintal (101·4 lb.) of nitrate, which is per ton :— £7, 6s. 8d. and £11, 9s. 2d.

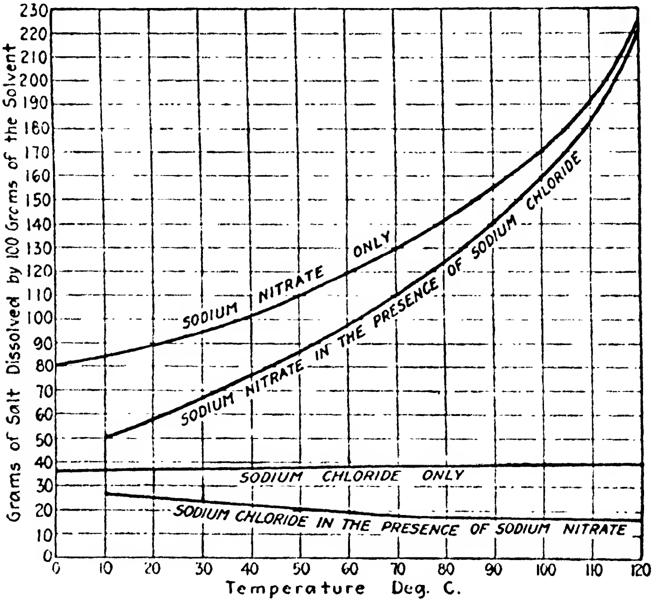

FIG. 16.—Solubility Curves of Sodium Nitrate and Sodium Chloride.

PRINCIPLES UNDERLYING THE SEPARATION OF NITRATE OF SODA FROM CALICHE.—In the Chilian nitrate industry material is put into the dissolving tank containing say, 15 per cent. of sodium nitrate and 20 per cent. of sodium chloride, and from the crystallising tanks sodium nitrate crystals of 95 to 96 per cent. purity, with only 1 to 2 per cent. of sodium chloride, are obtained.

The accompanying approximate curves (Fig. 16) will be found useful in interpreting these facts.

Solubility Figures for Sodium Nitrate and Sodium Chloride. —It is seen (1) that sodium nitrate is much more soluble in water than sodium chloride; (2) that increase in solubility with rise of temperature is much more marked with sodium nitrate than with sodium chloride; (3) that when the two salts are dissolved together at 120° C. the solubility of sodium chloride is considerably less than if no nitrate were present; and (4) that in cooling a solution saturated with both salts, only the nitrate is deposited since the solubility of the chloride increases with decrease of temperature.

With a mixture of sodium nitrate and chloride it is, therefore, possible to dissolve the two together at a high temperature, and on cooling to obtain crystals of nitrate without any deposition of chloride.

In practice the presence of other salts modifies the simple relations expressed by these curves, but the general trend of the solubilities is as shown. The crystallised nitrate may be contaminated by chloride in three ways, namely:—

1. By chloride in suspension carried over to the crystallising tanks.
2. By evaporation in the crystallising tanks being so great that the chloride solubility figure is exceeded and chloride separates out.
3. By the adherence of mother-liquor containing chloride to the crystals before drying.

The chloride may be reduced if desired by washing with a solution of nitrate.

The mother-liquor may circulate through the cycle for a long time, evaporation, mechanical and accidental losses of liquor being made up by fresh water as required. Only occasionally has it to be purged of impurities since normally, during the leaching process with rise of temperature, the chief impurity is deposited to such an extent that subsequent cooling does not cause its precipitation, and objectionable quantities of other soluble impurities take considerable time to accumulate.

The salts causing most difficulty as impurities are chlorates, perchlorates, and magnesium chloride and sulphate. Not only is difficulty experienced through deposition of these salts, but liquors rich in these salts, especially the latter two, have their solvent power for sodium nitrate diminished. In extreme cases the presence of excess of magnesium salts may mean that mother-liquor containing 30 per cent. sodium nitrate can not be used again.

BY-PRODUCTS.—1. *Potassium Nitrate* (see under this, p. 367).

2. *Potassium Perchlorate.*—The trade upper limit of toleration for perchlorate in sodium nitrate is 0·8 per cent., and it is necessary in working some caliches to eliminate some of this salt from the mother-liquors to ensure a sufficiently free nitrate. Although sodium perchlorate is exceedingly soluble, the potassium salt is very sparingly soluble and therefore perchlorate is eliminated by precipitation as the potassium salt. The solubility of potassium perchlorate is only 0·8 gr. per 100 grs. water at 0°C., and 21·7 grs. at 100°C., whilst in solutions containing large quantities of nitrate the figures are even lower.

3. *Iodine.*—After the leaching of a normal caliche has continued for several months, the sodium iodate content increases to about 9 grams of iodine per litre. At this stage it is convenient to extract the iodine by precipitation with sodium bisulphite solution. After removal of the iodine, the mother-liquor is again used for nitrate extraction.

Other Sources of Nitrate of Soda.

Many deposits of nitrate of soda have from time to time been chronicled from various parts of the world, but none have proved to be of commercial importance. Careful surveys of the Death Valley of California, where nitrate deposits are in existence, tend to show that the nitrate is not present in workable quantities.

Carriage.

When nitrate of soda in bags is being conveyed by rail, it is necessary to use closed vans or to cover the load with stout sheeting. Otherwise there is considerable danger of fire.

Storage.

The bag containing about 200 lb. of nitrate as shipped from Chili is a convenient unit to handle and store, but it is certainly safer to empty the nitrate from the bags immediately on receipt and store in bulk. Whether stored in bags or in bulk, nitrate should be housed in a fireproof building, and a sump should be provided on the floor to collect seepage, which is always present. A disadvantage of bulk storage is that the nitrate sets very hard in time and has to be dug out with picks.

Fire Danger.

Special attention must be directed to the desirability of keeping nitrate of soda as clear as possible from substances capable of taking fire. At one nitrate store which came under the author's notice, the nitrate bags were stacked on a layer of sawdust about one inch deep, presumably to absorb the seepage. This it certainly did. It also led to an outbreak of fire, caused, it was suggested, by a spark from a horse's shoe on the cobble-stone floor.

Nitrate of soda bags are impregnated with nitrate, and thus become practically incipient gunpowder. The merest spark is sufficient to set them on fire, and once alight the fire spreads rapidly, burns very fiercely, and is difficult to extinguish. This applies to full and empty bags alike, and great care should be exercised to protect them from fire. The safest plan with empty bags is to wash them thoroughly.

Treatment of Bags.

Nitrate of soda bags emptied in a normal manner contain up to 2 lb. of nitrate.

Shaking and Brushing.—By turning emptied bags inside out and *shaking*, much loosely adhering nitrate can be recovered (up to ½ lb. per bag). A further ½ lb. of nitrate can be removed by *brushing*. For convenience in hand brushing, easels with boards provided with hooks on which empty bags can be fastened, are found suitable. For large quantities, bag-brushing machines are useful and deal with nitrate bags rapidly and effectively. The brushing is conveniently carried out in the nitre storehouse.

Unwashed bags stored in bulk, especially in the open, are liable to destruction by spontaneous combustion. It is advisable, therefore, not to store emptied bags any considerable time until they have been washed free of nitrate.

Washing.—The extraction of nitrate from emptied bags is a very simple operation and is certainly a rational and economical proceeding. On a small scale, water heated by waste steam may be used for dissolving the nitrate. The bags from the dissolving tank are rinsed in one or two waters, wrung by mangle or centrifugal and dried normally in the air, or by waste heat. The nitrate liquor is concentrated and the nitrate crystallised and drained.

In dealing with large quantities of bags, a special plant may be provided for washing. Such a plant should comprise boiling tanks, rinsing tanks, centrifugals, driers, a film evaporator, crystallising tanks, nitrate draining racks, and necessary accessories. Plants such as here outlined have handled hundreds of thousands of nitrate bags during the war, with a recovery of 1 lb. to 2 lb. of nitrate per bag, and providing clean bags containing less than 1 oz. of nitrate per bag.

Drying.

Chilian nitrate has an average water content of 2 to 2½ per cent. In the manufacture of nitric acid from this nitrate, particularly if highly concentrated acid is required, it may be considered desirable to reduce the moisture content before acting on it with sulphuric acid (see p. 154).

It is common practice in small works to utilise the heat of the cover plates over the nitric acid retorts for drying purposes. A charge of nitrate is spread on the top plate during working, and some degree of drying is thus effected. This practice is not to be recommended as the tops of retorts should, if possible, be kept quite clear for effective working conditions. If other and more suitable sources of waste heat are available partial drying of the nitrate may be effected on hot iron plates.

Drying machines are often installed where large quantities of nitrate have to be dealt with, and the drying of nitrate in these machines may be done economically. Nearly any form of rotary drier is suitable, but the Cummer drier, which has been much used, may be taken as typical. It consists essentially of a sloping revolving trommel carrying nitrate and built in the flue of a fire. A current of heated air is drawn by a fan placed in the air exit flue, first round about and then through the trommel. Moist nitre is fed through crushing rolls to the well of a bucket elevator which delivers to the high end of the trommel. As the nitrate passes slowly down the trommel it meets the heated air passing from the fire to the fan, and by the time the nitrate is delivered at the bottom end to a second bucket elevator, lifting to a store bin, its moisture content may be reduced to less than 0·5 per cent. Two important factors determining efficiency of drying are the size of nitrate crystal fed to the trommel and the volume of heating air used.

Dried nitrate is much nicer to handle than moist nitrate.

Analysis.

A reasonably complete analysis of commercial nitrate of soda is obtained by determining the following constituents, moisture, insoluble matter, nitrate, potassium, chlorides, perchlorates, sulphates, and iodates. A scheme for carrying out such an analysis is given below.

For routine work this scheme can often be cut down to determining moisture, nitrates, and chlorides.

Moisture.—About 5 grams are accurately weighed in a small silica crucible and heated gently over a Bunsen flame until the nitrate just fuses. The crucible is then cooled in a desiccator and reweighed, and the percentage of moisture in the sample calculated from the loss in weight.

Insoluble Matter.—Ten grams are dissolved in distilled water, and the whole washed through a filter paper which has previously been dried for one hour at 105° C., and weighed in a stoppered weighing-bottle. After several washings with distilled water the filter paper and the insoluble residue are dried in an air-oven for one hour at 105° C.

The result is expressed as percentage of insoluble matter in the sample as received.

Nitrates.—For the determination of nitrates a portion of the sample is partially dried, as it is difficult to obtain a representative sample from the powdered wet material. For this purpose about 100 grams are partially dried by heating in an air-oven for two hours at 105° C. The nitre is then quickly powdered in a mortar and transferred to a stoppered bottle, which is kept in a desiccator; the actual percentage of moisture in this material is determined as described above, and the results are finally calculated back on the sample as received.

About 0·4 gram of the dried sample, accurately weighed in a small weighing-bottle, is emptied into the dry cup of a nitrometer and washed in with 1·5 c.c. of distilled water. Fourteen c.c. of 94·5 per cent. H_2SO_4 are then measured out in a graduated cylinder; 8 c.c. of this acid are used in four successive portions of 2 c.c. each for washing down the cup, and the remaining 6 c.c. are then added and the cup well drained into the nitrometer. Decomposition is effected by shaking for two minutes under suction, after which the tube is set up and approximately levelled and allowed to cool. After half an hour (or more) the tube is accurately levelled by raising or lowering until, on cautiously opening the tap, the contained drop of sulphuric acid shows no movement. This condition is best approached from the suction side. The volume is then read, and the temperature of a thermometer suspended in close proximity to the nitrometer observed to the nearest tenth of a degree. The barometer is then adjusted and read, the temperature as recorded by the attached thermometer being observed before touching the instrument.

The volume of gas in the nitrometer is then re-read, first trying the tap to see whether the gas is still in equilibrium, and making any adjustments which may be found necessary.

Thermometer and barometer readings are corrected according to standard certificates, and special barometric corrections for latitude, capillarity, and temperature of mercury and scale applied.

After correcting the volume of nitric oxide to N.T.P. the percentage of sodium nitrate in the dried sample is calculated, and a "solubility" correction applied to correct for the solubility of nitric oxide in sulphuric acid.

Under the conditions of the test, this amounts to 0·4 per cent. of the percentage of sodium nitrate found, *i.e.*, if the sample shows 96·4 per cent. $NaNO_3$, the solubility correction will amount to 0·4 per cent. of 96·4 or 0·38, and the result returned will be 96·8 per cent.

Potassium.—Ten grams are evaporated to dryness with HCl several times, in order completely to convert the salts to chlorides. The mass is then dissolved in distilled water, and the potassium determined by the following method.

Hydrochloric acid gas is conducted into the solution which has been concentrated as much as possible, until it has become saturated with the gas (the lower end of the delivery tube should be enlarged, and should just touch the liquid). To every 100 c.c. of the solution 2 c.c. of water are now added, the precipitated sodium chloride is allowed to settle, and the solution poured through a funnel provided with a platinum filter-cone. The precipitated salt is washed three times by decantation with 95 per cent. alcohol, transferred to the funnel, dried by suction, and then washed three times more with alcohol.

In the solution there remains all the potassium, some sodium, and possibly calcium, magnesium, and sulphuric acid.

The solution is evaporated to dryness on the water-bath, if possible (or if sulphuric acid is present, the last traces of the free acid are removed by means of the free flame), the residue is weighed, for every decigram of the salt mixture 3 c.c. of twice normal hydrochloric acid are added, with more than enough chloroplatinic acid to precipitate all the potassium, and the liquid is evaporated to a paste. It is then treated with 20 c.c. of absolute alcohol, and well stirred. After standing five minutes, 5 c.c. of ether are added, the mixture is allowed to stand half an hour under a bell-jar and then filtered. As the residue often contains small amounts of other chloroplatinates, it should be purified as follows:—The precipitate is allowed to dry in the air, it is dissolved in a little hot water, a few drops of chloroplatinic acid are added, and the above operation is repeated. The precipitate thus obtained contains all of the potassium in the presence of some sodium chloride, and possibly sodium sulphate. It is washed with a mixture of ether and alcohol until the liquid runs through the filter completely colourless, after which the precipitate is dried, moistened with hot water, and digested on the water-bath with a few drops of chemically pure mercury, constantly stirring with a glass rod until the liquid appears perfectly colourless.

By means of this treatment the potassium chloroplatinate is completely decomposed with separation of platinum:—

$$K_2PtCl_6 + 4Hg = 2KCl + 2Hg_2Cl_2 + Pt.$$

The mixture is thoroughly dried on the water-bath and gently ignited until the mercury is all volatilised; the platinum is changed at the same time to a denser form, which can be readily washed by decantation. After cooling, the mass is treated with water, and the residual metal is washed with hot water, dried, and cautiously ignited. The filter is ignited in a platinum spiral, its ash is added to the main portion of the platinum in the crucible which is now ignited, and weighed. The weight obtained multiplied by 0·7612 gives the amount of potassium chloride, or, multiplied by 0·3994, gives the corresponding amount of potassium.

The digestion of the potassium chloroplatinate with mercury is carried out in a silica basin.

Note.—A much simpler and more rapid method is adopted in the laboratories of Messrs Brunner, Mond, & Co., where potassium is precipitated as potassium cobalti-nitrite in special tubes, which are then centrifuged and the precipitates compared with standard samples.

Chlorides.—Ten grams are dissolved in distilled water, and the solution titrated with decinormal silver nitrate solution, using potassium chromate as indicator. The chloride is calculated as percentage of sodium chloride (NaCl) on the sample as received.

Perchlorates.—A mixture of 10 grams of the sample with 2 grams of cupric oxide is fused in a nickel crucible for twenty minutes. When cold, the fused mass is treated with distilled water, and the aqueous extract is titrated with decinormal silver nitrate solution, using potassium chromate as indicator. The perchlorate equivalent of the chloride corresponding to the difference between the value obtained by this test and that obtained in the foregoing test is calculated, and after correcting for any iodate which may be present, the result is expressed as percentage of potassium perchlorate in the sample as received.

Sulphates.—Ten grams are boiled with distilled water and the solution filtered. The filtrate is again raised to boiling-point, and any sulphate present precipitated by the addition of 10 c.c. of warm 10 per cent. barium chloride solution. The whole is kept warm on a sand-bath for one hour in order to granulate the precipitate. The liquid is then filtered, and the precipitate washed free from chlorides, and finally ignited in a silica crucible.

After complete incineration of the filter paper, one drop of H_2SO_4 and one drop of HNO_3 are added to the precipitate before the final ignition. The result is calculated on percentage of sodium sulphate on the sample as received.

Iodates. — A mixture of 10 grams of the sample with 2 grams of cupric oxide are fused in a nickel crucible for twenty minutes. When cold, the fused mass is extracted with distilled water, and the solution acidified with acetic acid. It is then transferred to a separating funnel, and a few cubic centimetres of copper sulphate solution added and thoroughly mixed with the solution. Twenty c.c. of chloroform are then added, and the whole well shaken. The chloroform layer is washed with distilled water, and finally titrated with decinormal sodium thiosulphate solution until the pink colour is discharged; usually only a trace of iodate is present, so that no more than one or two drops of the thiosulphate solution are required. The chloroform layer contains only half the iodine content of the iodate present in the sample.

If there is an appreciable quantity of iodate present, the requisite deduction is made from the value obtained for perchlorates.

Note. — **The Refraction Method.** — It was formerly very common in the nitrate of soda trade to estimate the value of the nitrate by the "refraction" method. In this method, 10 grams are well dried in a porcelain crucible, weighed again, dissolved, the residue (if any) is estimated, the liquid diluted to a certain volume, and in separate portions of the liquid the chloride and sulphate are estimated in the usual way. The sum total of moisture, insoluble matter, sodium chloride, and sodium sulphate is called the "refraction," and it is assumed that the remainder is real sodium nitrate. This may, however, lead to very erroneous results, where, for instance, the nitrate contains some potassium nitrate. The presence of perchlorate also causes errors, and it is clear that the "refraction" method can not give a true figure for the nitrate content. This must be obtained by direct determination.

Nitrate Determination by Devarda's Method.—Weigh out 10 grams of the sample and dissolve in 300 c.c. of warm water in a calibrated 500 c.c. flask. Cool and make up to 500 c.c. Take 25 c.c. of the well-mixed solution (=0·5 gram nitre) for the determination, and introduce it into a Kjeldahl flask of 500 to 650 c.c. capacity. Add 300 c.c. of water, 3 grams of Devarda's alloy (passing a 20-mesh sieve), 50 c.c. of caustic potash solution (S.G. 1·3), and connect at once with the distilling apparatus, such as is used for Kjeldahl estimations, and distil the ammonia into semi-normal sulphuric acid solution. Butt[1] specially recommends the use of the Davisson scrubber bulb[2] for this distillation. Before the distillation apparatus is required for use, 20 to 30 c.c. of water are drawn into the scrubber bulb. The reduction and distillation are carried on together, the solution in the reaction flask being boiled at such a rate that 175 to 200 c.c. of distillate are collected in an hour, by which time the whole of the ammonia will be distilled over. With the distillation half completed, the heating should be discontinued for a short time to allow a portion of the condensate in the scrubber bulb to flow back into the distilling flask. The ammonia collected in the $\frac{N}{2}$ sulphuric acid solution is estimated in the normal way, using methyl red as indicator.

The following two analyses of commercial nitrate of soda are given by Butt[3]:—

H_2O	3·08	2·74
Insol.	0·21	0·26
Na_2SO_4	0·27	0·33
NaCl	0·51	0·56
$NaClO_3$	0·05	0·05
$NaClO_4$	0·94	0·51
Fe_2O_3 Al_2O_3	0·10	0·09
CaO	0·09	0·07
MgO	0·18	0·10
$NaIO_3$	0·05	0·04
P_2O_5	0·04	0·06
KNO_3	3·48	2·55
$NaNO_3$	90·98	92·57

Statistics.

Historical.—The following brief survey of the early history of Chilian nitrate is from W. Montgomery & Co.'s half-yearly report at the close of 1900.[4]

Our earliest trade information regarding nitrate of soda is

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[1] *J. Ind. Eng. Chem.*, 1920, **12**, 352-354.

[2] *J. Ind. Eng. Chem.*, 1919, **11**, 465-466.

[3] *J. Ind. Eng. Chem.*, 1920, **12**, 354.

[4] *J. Soc. Chem. Ind.*, 1901, **20**, 84.

derived from a circular issued by Mr Alfred Bourne, in January 1841, in which Mr Bourne reviews the business of the previous ten years, and tells us that imports into England in 1831 amounted to 100 tons, the price at that date being 28s. per cwt.; that the imports gradually increased during the decade, reaching 7200 tons in 1840, with a price of 20s. 6d. per cwt.; that the increase was chiefly for agricultural purposes, and also that there were symptoms of demand from Scotland and for transhipment to France.

For the twenty years ending with 1860, progress in consumption was very slow, reaching to 50,000 tons, nearly the whole of which was used in the British Isles. During the next decade these figures had little more than doubled, the quantity being about equally distributed between the United Kingdom and the Continent.

From 1870 to 1875, with remunerative prices for cereals in England, the consumption rapidly rose, until in the latter year it reached 165,000 tons in the United Kingdom and 132,000 tons on the Continent. For the next twenty-two years, until 1897, there was an almost unbroken record of greatly reduced deliveries. It was in the year 1879 that the relative positions of the United Kingdom and Continent began to change as regards consumption, and the latter speedily and irretrievably left the former far behind.

Nitrate of soda has, from time to time, suffered serious mishaps. In 1868 a terrible earthquake and tidal wave overtook and destroyed Iquique, causing great havoc to the nitrate industry, and producing in Europe violent changes in price. In 1877 Peru was again visited with a similar calamity, although not so disastrous. This was followed in 1879 by the outbreak of war between Chili and Peru, which lasted over twelve months, and its effect upon the nitrate shipments was very serious. In the end the whole of the rich nitrate districts which belonged to Peru passed into the possession of Chili. For a few years preceding this war Peru had been expropriating the nitrate fields. When Chili took possession, she adopted the policy of permitting the private owners to work their own deposits, the Government merely imposing an export duty of about £2, 12s. 6d. per ton, and this system has continued down to the present date.

One consequence of the curtailed shipments, caused by the war between Chili and Peru, was to raise the price in Europe from 13s. per cwt. to 19s. 6d. per cwt., and the following season the European farmer used 30 per cent. less than the previous year

With a recurrence to more moderate prices and a great stimulus in agriculture on the Continent, especially in the cultivation of beetroot, a vast increase in the consumption of nitrate was noticeable in the decade ending with the year 1890.

The figures during that period for the Continent grew from 113,000 tons to 666,000 tons. In the United Kingdom during the same time, owing to agricultural depression, caused chiefly by the disastrously low price of cereals and the consequently reduced acreage under cultivation, especially of wheat, the consumption fluctuated between about 70,000 tons in 1880 to 120,000 in 1890. From 1890 until to-day, the record of consumption throughout the world is one of almost unbroken advance, slow perhaps, but of such uniform steadiness that there is every reason to believe that it is of a staying character. The following figures will show at a glance the total progress made during the periods to which we have referred:—

Year.	World's Consumption, Tons	Price on 31st December, per Cwt.	
		s.	d.
1831	100	28	0
1840	7,200	20	6
1860	50,000	15	0
1870	103,000	15	9
1880	228,000	14	3
1890	885,000	7	7½
1900	1,324,000	8	6

Cost.—The pre-war cost of production at a medium-sized modern nitrate factory, including all factory expenses in Chili—such as labour, fuel, repairs, bagging, freight to port, shipping charges and commission, amortisation of the cost of the nitrate grounds and plant, interest on capital at 5 per cent., and Chilian export duty at 2s. 4d. per Spanish quintal (101·4 lb.), amounted to 7s. 4d. per quintal of nitrate f.o.b. in Chili, or £8, 1s. 4d. per ton (95 per cent. purity). The expenses incurred in marketing the product in Europe, including sea freight at £1, 5s. per ton, loss in weight during the voyage, landing charges and port dues, increased the cost to £10, 4s. per ton free on shore in England.

The average cost f.o.b. Chili in 1920 was 12s. per quintal, or £13, 4s. 10d. per ton.

Production, Exports, and Market Prices.

Year.	Production, Tons.	Exports from Chili, Tons.	Average Annual Market Price of 95% Nitrate in Liverpool, per Ton.		
			£	s.	d.
1903	1,429,150	1,426,275	9	10	10
1904	1,421,580	1,471,328	10	4	2
1905	1,543,120	1,652,286	10	16	10
1906	1,639,300	1,690,400	11	6	8
1907	1,646,890	1,619,426	11	3	4
1908	1,733,540	1,906,423	10	4	2
1909	1,922,000	2,087,579	9	15	0
1910	2,251,000	2,285,156	9	7	6
1911	2,313,450	2,396,265	9	17	11
1912	2,485,860	2,438,885	11	1	8
1913	2,729,124	2,678,810	11	1	8
1914	2,424,969	1,807,636	10	6	8
1915	1,735,382	1,979,325	12	12	11
1916	2,867,868	2,937,535	17	12	6
1917	2,965,284	2,724,757	24	12	6
1918	2,795,740	2,885,923	26	10	0
1919	1,645,640	918,747	20	10	0
1920	2,494,696	2,762,177	24	2	6

World's Pre-war Consumption of Chili Nitrate.

Country.	Quantities in Metric Tons of 2204 lb.		
	1911.	1912.	1918.
Germany . .	743,412	911,962	833,112
U.S.A. . . .	568,136	441,047	589,187
France . . .	338,706	354,517	327,192
Belgium . . .	303,780	309,817	318,515
Holland . . .	144,652	180,924	164,502
United Kingdom .	132,931	137,415	128,561
Italy . . .	53,616	44,545	51,690
Egypt . . .	19,018	23,981	25,638
Spain . . .	8,977	13,554	13,150
Austria-Hungary .	5,281	7,114	7,445
Denmark . .	3,438	4,825	10,748
Switzerland . .	2,371	5,198	...
Other countries .	77,074	95,746	87,233

From "Final Report, Nitrogen Products Committee," H.M. Stationery Office, 1919.

It is estimated that the world's consumption for agriculture is 75 per cent. of the total.

REFERENCES.

Chili Nitrate Industry.

Montgomery & Co.—*J. Soc. Chem. Ind.*, 1901, **20**, 84.

Hobsbawn.—*Met. and Chem. Eng.*, 1917, **16**, 253-59.

Nauchkoff.—*Met. and Chem. Eng.*, 1917, **17**, 525-36.

Allen.—*Eng. and Min. J.*, 1917, **103**, 230-33; *J. Amer. Chem. Soc. Abstr.*, 1917, **11**, 1020.

Hobsbawn and Grigioni.—*J. Soc. Chem. Ind.*, 1917, **36**, 52-63.

Allen.—*Min. Sci. Press*, 1918, **116**, 522; *J. Amer. Chem. Soc. Abstr.*, 1918, **12**, 1412.

Irvin.—*Min. Sci. Press*, 1918, **117**, 109-10; *J. Amer. Chem. Soc. Abstr.*, 1918, **12**, 2043; *Eng. and Min. J.*, 1919, **107**, 265-67; *Amer. Inst. Min. Eng.*, 1918, **134**, 505-22.

Marco.—*J. Ind. Eng. Chem.*, 1919, **11**, 780-81.

Donnan.—*Chem. Age*, London, 1919, **1**, 634-35.

Bertrand.—*Chimie et Industrie*, 1920, **3**, 3-18; *Chem. and Met. Eng.*, 1920, **22**, 655-59; 1207-11,

The Chilian Nitrate Industry, by Alejandro Bertrand, and issued by the Chilian Nitrate Committee, Friars House, New Broad Street, London, E.C., gives a full set of references to Chilian nitrate literature, including patents, up to 1919.

The recently introduced monthly review entitled *Caliche* gives a bibliographical index in vol. i., April 1919, and subsequent numbers of this publication give full particulars of later work.

Allen.—"The Recovery of Nitrate from Chilian Caliche." (Griffin.)

Allen.—"The Donnan Programme of Investigation for the Chilian Nitrate Industry"; *Chem. and Met. Eng.*, 1922, **27**, 1121.

Chilian Nitrate Committee.—"Report on a Programme of Investigation for the Chilian Nitrate Industry, by Professor F. G. Donnan."

Partington and Parker.—"The Nitrogen Industry," 1922.

Perchlorates.

Monnier.—*Arch. Sci. Phys. Nat.*, 1916, **42**, 210-16.

Analytical (Caliche).

Clennell.—*Eng. and Min. J.*, 1918, **106**, 660-63; *J. Amer. Chem. Soc. Abstr.*, 1919, **13**, 16.

OTHER DEPOSITS.

CALICHE DEPOSITS OF ATACAMA.—*Eng. and Min. J.*, 1917, **108**, 1059-60; *J. Amer. Chem. Soc. Abstr.*, 1917, **11**, 2317.

WILLIAMS.—*Min. Sci. Press*, 1918, **117**, 285-89; *J. Amer. Chem. Soc. Abstr.*, 1918, **12**, 2181.

SODIUM NITRATE.

Drying.

PRIDEAUX.—*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 182·85.

LOWRY AND HEMMINGS.—*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 104.

Fires.

LOOS.—*Arch. Suikerind*, 1918, **26**, 1893-95; *J. Amer. Chem. Soc. Abstr.*, 1919, **13**, 2738.

CHAPTER II

THE MANUFACTURE OF NITRIC ACID FROM CHILI SALTPETRE AND SULPHURIC ACID

THE REACTION INVOLVED.

THE production of nitric acid by distilling sodium nitrate with sulphuric acid is an essentially simple problem, and the reaction involved may be represented by the following equation—

$$\begin{aligned} \text{(A)}\quad 2NaNO_3 + H_2SO_4 &= Na_2SO_4 + 2HNO_3 \\ \underbrace{2 \times 85}_{} + 98 &= 142 + \underbrace{2 \times 63}_{} \end{aligned}$$

The volatile nitric acid is displaced from the system and may readily be condensed, while sodium sulphate remains in the reaction vessel.

In practice it is not advisable to work with the materials in the proportions indicated above, because

1. The temperature required to complete the reaction is very high (approx. 900° C.), and to work at such a high temperature would involve the following serious disadvantages :—

(*a*) Heavy wear and tear on the apparatus used.

(*b*) High fuel consumption.

(*c*) Loss of product due to decomposition of nitric acid,

$$\begin{aligned} 4HNO_3 &= 2H_2O + 4NO_2 + O_2 \\ 2HNO_3 &= H_2O + NO + NO_2 + O_2. \end{aligned}$$

(*d*) High nitrous acid content in the nitric acid produced, due to the above decomposition and to the reaction represented by the following equation—

$$H_2O + 2NO_2 = HNO_3 + HNO_2.$$

(*e*) Production of weak nitric acid owing to decomposition (*c*).

2. The resulting sodium sulphate (Mp. 860°) would readily set hard at the completion of the reaction and would be difficult to remove from its containing vessel.

By sacrificing a portion of the sulphuric acid represented in equation (A) and working more nearly to the following equation—

$$\text{(B)}\ NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$
$$85 + 98 = 120 + 63$$

the temperature for completion of the reaction need not exceed 200° C., and the residue remains sufficiently fluid to permit its being run freely from the reaction vessel.

The reaction represented by equation (A) involves the use of $NaNO_3$ and H_2SO_4 in the ratio 85 : 49, while the ratio for equation (B) is 85 : 98.

In modern practice the charges of nitrate of soda and sulphuric acid are so adjusted that the proportions of $NaNO_3$ and H_2SO_4 are approximately 85 : 80. The residue, therefore, is a mixture of sodium hydrogen sulphate and sodium sulphate. It is known as "Nitre Cake."

PLANT REQUIRED.

Nitric acid production is a distillation process, and the plant necessary consists of a distilling vessel (retort), condensing system, and receiving vessel.

HISTORICAL.

The following account of the early manufacture of nitric acid is reproduced from a paper by Oscar Guttmann.[1]

NITRIC ACID.—Nitric acid seems to have been known in the earliest times. It is said that the black drawings on the clothes of mummies were made with silver nitrate, but the first description of the production of nitric acid (aqua dissolutiva, aqua fortis) is given by Geber in 778, who made it by distilling nitre with copper sulphate and alum. Raymond Lullius, in the thirteenth century, made it from nitre and iron sulphate, and Glauber, in 1648, taught us to make it from nitre and oil of vitriol. In 1759 it was still made, according to Neumann, by

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[1] *J. Soc. Chem. Ind.*, 1901, **20**, 5-8.

charging a tubulated retort placed on sand with powdered nitre, luting on a large receiver, and pouring in oil of vitriol in small quantities through the tubulure.

Mr Sheffield's[1] manuscript of 1771 gives many details about the manufacture on a large scale. The general arrangement is shown in Fig. 17; but instead of reproducing each part of the apparatus singly, as drawn by him, I have preferred to put them together, so that the function of each can be seen at a glance.

The retort was an iron pot *a* (Fig. 17), holding 37½ galls. and weighing 20 cwt. It could take a charge of 200 lb. of nitre and 104 lb. of oil of vitriol; thus neutral sulphate was aimed at, which was called "sal enixum." The pot was closed by a pothead *b*, with two arms "made at Vauxhall" from earthenware. Each of these arms was connected to a condensing plant. This consisted of a kind of crosspiece called the pipe receiver, which was surmounted by a "balloon" or large globe receiver holding 60 galls. The lower part was luted to a "perpendicular receiver" *e*, and the arms to "large common receivers" *f f*, holding 30 galls. each. The latter rested on "bosses" *g*, made of twine. The luting was made of equal parts of clean sand and "hufcap," a kind of clay, with one-quarter part of "sal enixum" and some water.

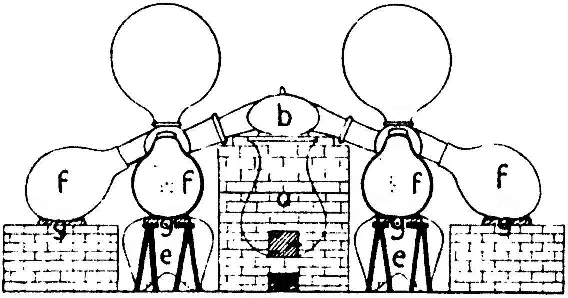

FIG. 17.—Ancient Retort and Condensers.

The distillation lasted four days. Towards the end the fire was raised "intensely high." The consumption of coal was

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[1] W. E. Sheffield, a chemist who lived in Birmingham from 1771 to 1790 (the dates occurring in the manuscript).

5 cwt., and the production 200 lb. of "gilders' aqua fortis" (1·375 sp. gr.; see later on), which works out at about 96½ per cent. of the theoretical yield.

The cost of production works out as follows:—

	£	s.	d.
200 lb. of nitre at 70s. per cwt. . . .	6	5	0
104 lb. of O.V. at 3¾d. per lb. . . .	1	15	1
5 cwt. of coal at 5d. per cwt. . . .	0	2	1
For 200 lb. of gilders' acid . .	8	2	2

Cost without labour, per lb., approximately, 9¾d.

It will be noticed that the distillation of a 200 lb. charge lasted four days, which is explained by the fact that the condensing plant had no vent for the uncondensed gases, and had therefore to be worked very slowly.

There were many kinds of aqua fortis sold, which are enumerated in the following table:—

	Weight.		Spec. Grav.	Price per lb.	
	oz.	dr.		s.	d.
Pure spirit of nitre . . .	23	12	1·485	3	6
Gilders' aqua fortis . . .	22	0	1·375	1	8
Brass-founders' aqua fortis . .	24	0	1·500	1	8
Syers' (assayers') aqua fortis Refiners' aqua fortis . .	20	0	1·250	1	3
Best platina	24	15	1·559	1	1
Single aqua fortis, or weak platina	23	0	1·437	0	10
Twelve-penny aqua fortis . .	24	6	1·523	1	0

Some explanation for this table is, of course, necessary, and given. The various receivers had generally some water put in before starting, but if no water was put into the perpendicular receiver, then "pure spirit of nitre" was obtained. If, on the other hand, 10 lb. of water were put into it, then gilders' acid resulted; and if this was not up to standard, pure spirit of nitre was added, whilst if too strong weak aqua fortis or water was used for dilution. Gilders' acid is the most useful, because most other sorts are made from it by mere mixing.

For making syers' and refiners' aqua fortis, 30 lb. of water are put into each of the other receivers, and the various acids mixed together.

Brass-founders' aqua fortis is made by mixing 60 parts of gilders' aqua fortis with 10 parts of oil of vitriol. The manuscript naïvely adds: "Sells for 20 pence, the same price of gilders', tho' lowered with one-sixth of oil of vitriol; this justly esteemed a very particular secret in this branch of business."

Platina aqua fortis is made from 16 parts of gilders' acid and 40 lb. of oil of vitriol lowered to 25 oz. "It is used for best dip for platina."

Single aqua fortis, or weak platina, is made from 16 lb. of gilders' acid brought down to 21½ oz., and 40 lb. of oil of vitriol lowered to 24½ oz. "Used for the first dipping of platina work."

Twelve-penny aqua fortis is the same as the weak platina only the gilders' acid is of the proper strength. It is also used for finishing platina.

The manuscript also contains an account of the manufacture of nitric acid in glass retorts, 9 in. diameter, 12 in. high, and called quart retorts, which were made by Stocks, near Blackfriars Bridge, and could be charged with 14 lb. of nitre. The coal consumption was excessively high — about 11 lb. per pound of gilders' acid; yet there was a profit of about 25 per cent.

Improvements in plant for the manufacture of nitric acid were made in recent years only. Plain pots can still be found in some factories, and the condensing plant is also frequently of a very primitive nature.

RETORTS.

Types.

Nitric acid was formerly made both in iron and glass retorts, but nowadays cast-iron retorts are universally employed. Early large scale cast-iron retorts were cylinders, and were supported horizontally in the flue of a fire. The ends of the cylinder were closed by thick cast-iron or sandstone discs, luted.in and held by iron bars pressing against them on the outside. Sometimes one end of the cylinder remained permanently closed, but the other end had to be removed either entirely, or if so arranged, in part for charging nitrate and discharging nitre cake. More often both ends were removable.

An outlet pipe for the nitric acid vapours was provided at the top near to the closed end of the cylinder, and an opening

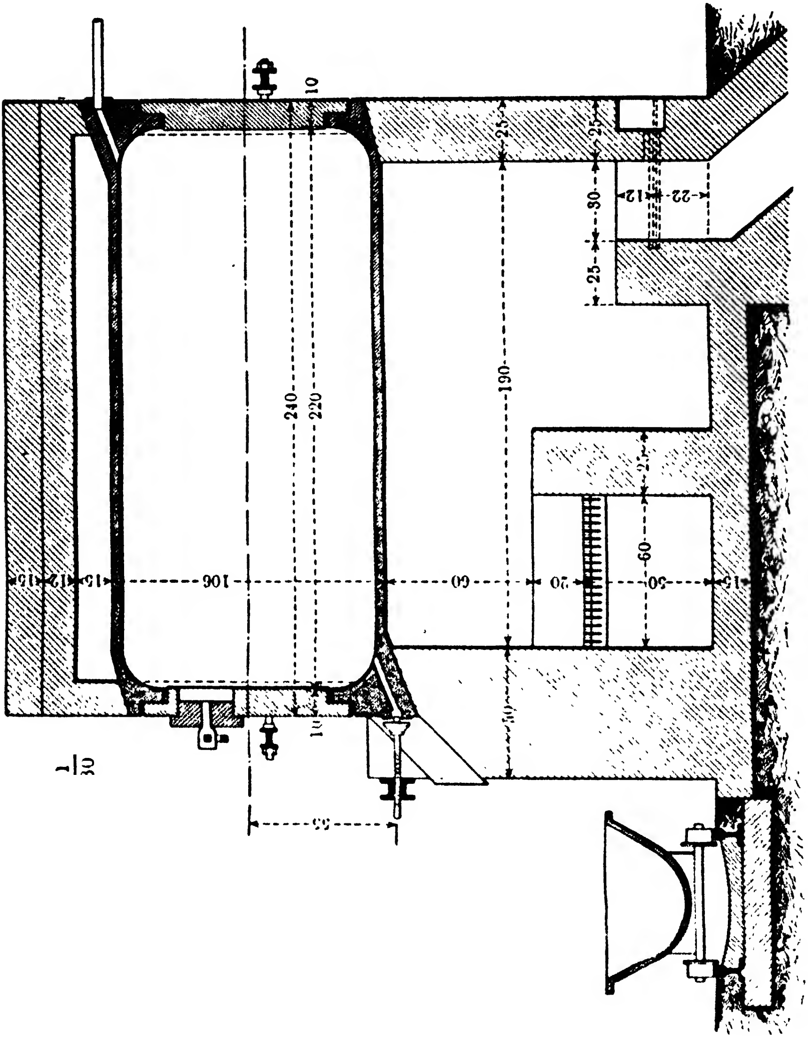

FIG. 18.—Horizontal Retort—Longitudinal Section.

in the removable end or in the top of the cylinder allowed the introduction of sulphuric acid.

Originally with cast-iron cylinders the ratio of sulphuric acid to nitrate approximated more to equation (A) p. 38, and at the completion of a distillation it was customary to have to dig out the nitre cake. Later, more fluid nitre cakes were made by using more acid, and provision was made, by having a hole capable of being plugged in the charging end of the retort, for running out the nitre cake.

Finally, the practice with these retorts was essentially that now common with modern retorts, but very few cylinder retorts are now in use, practically all having been superseded by the pot type which requires much less manual labour, although in the Uebel process a reversion to cylinders has taken place.

An interesting nitric acid retort was developed in the early stages of the recent war by Mr W. C. Wakefield at his works at Savile Town, Dewsbury. Finding it difficult to obtain normal nitric acid plant and having on hand a number of saltcake pots, he built these into retorts by providing brick domes. They worked admirably, but naturally the brick domes were not long lived.

The pot type of retort has developed from a cylindrical vessel set vertically in the flue instead of horizontally. The following description of an early pot type of retort is from Vol. I. of the 4th Edition of Lunge's work.

The former kind, as employed in France for very strong nitric acid, is shown in Fig. 19. It consists of cast-iron pots of from 4 to 5 ft. diameter and equal height, and a metal thickness of 1¾ to 2 in. (rather thicker at the bottom). There is a wide neck *a* at the top, closed by a lid, fastened on with a suitable cement, *e.g.* a mixture of clay and gypsum. There is a tube *b* for carrying away the gas, either coming out perpendicularly at the top, as shown here, or bending away horizontally, as in a laboratory retort; this tube should be lined with an earthenware tube as far as it is at all liable to cool down below the point where the metal can be acted upon by nitric acid Another tube *c* serves for introducing the sulphuric acid; this is preferable to running it in through the neck *a*, after charging the nitre. Sometimes there is no pipe provided for running out the liquid residue, but it is better to have one, as shown at *d*, and to protect this tube against the direct action of the fire by a fireproof covering. Where this is not provided, the liquid residue must be ladled out through *a* at the close of the operation, which is a disagreeable proceeding. The pot is set in a furnace so that it is altogether surrounded by the fire, even

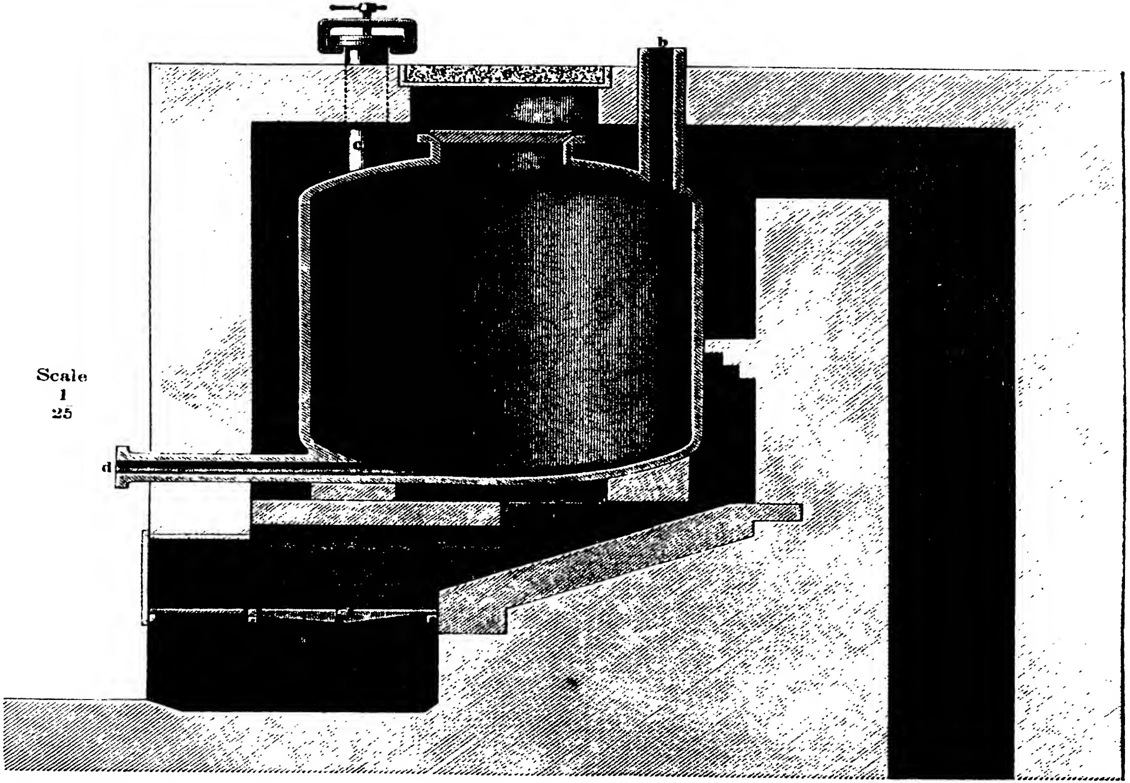

FIG. 19.—Early Pot Retort.

[Face page 44.

at the top, to which access is afforded for charging by lifting off a fire-clay slab, or a metal plate filled with ashes, as shown at *e*. By this means a saving of fuel is effected, and the equal heating of the retort causes it to stand the action of the nitric acid very well. A pot 5 ft. wide and 5 ft. high takes a charge of 9 cwt. of nitre, and requires from sixteen to eighteen hours to work this off, including the time for charging and emptying. Of this time, one hour may be reckoned for charging and making the joints, six hours for the first stage, where red fumes appear, about as much for the second stage, where the vapours are almost colourless, and four or five hours for the last stage, where the temperature has to be raised much higher, the yellow and red vapours appear again and more water comes over with the acid.

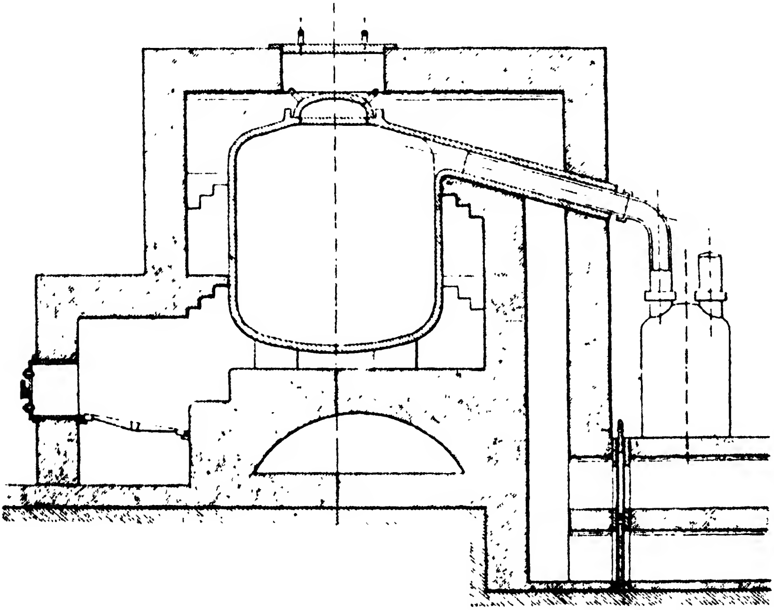

FIG. 20.—Early Pot Retort with Wheel Flue.

Fig. 20 shows another pot of this period with a wheel flue. Provision is made for by-passing some of the flue gases under the condensing jars.

Figs. 21-23 serve to show various forms of the pot type of retort in common use, the most recent design being the Waltham retort, Fig. 23. Points of support are provided in the form of lugs which are cast on the outside of the retort body.

The Guttmann Retort.—This retort is seen to be in three sections, the lower section having an outlet pipe for the discharge of nitre cake and the upper section having charging and vapour delivery openings. The two upper sections rest in sockets into which they are firmly cemented by rust joints (see p. 127). Internal flanges are cast on the two upper sections, and these serve to direct an inward flow when there is a surging of the contents of the retort.

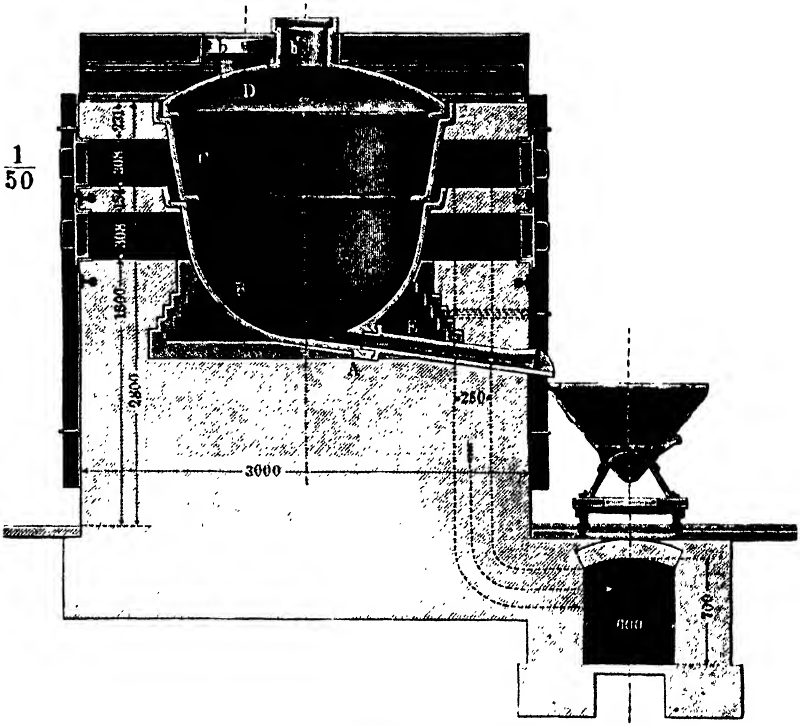

Fig. 21.—The Guttmann Retort.

The Valentiner Retort.—This retort is very flattened at the base. It does not have a middle section nor internal flanges.

The Waltham Retort (with extension ring).—This retort is used either with or without middle section (or extension ring). It is very similar to the Guttmann retort, having socket joints and internal flanges, but it has vertical sides, a flatter bottom, and an additional casting for charging lid and vapour take-off pipe.

Retort with False Bottom.—An interesting retort was developed at H.M. Factory, Gretna, and patented by J. Prentice,[1] as an effort to reduce expenditure consequent upon the necessity of replacing retorts which cracked in process. The replacement of a nitric retort is a rather big matter and involves the removal of one front of the brick setting. To obviate this, the idea of having a loose bottom to the retort was suggested and the design introduced by Prentice is shown in Figs. 24 and 24A, the drawings being self-explanatory. The retort bottom was fixed in the following manner: Two strips of $\frac{5}{8}$-in. blue asbestos cord were soaked in silicate of soda solution to make a joint for the

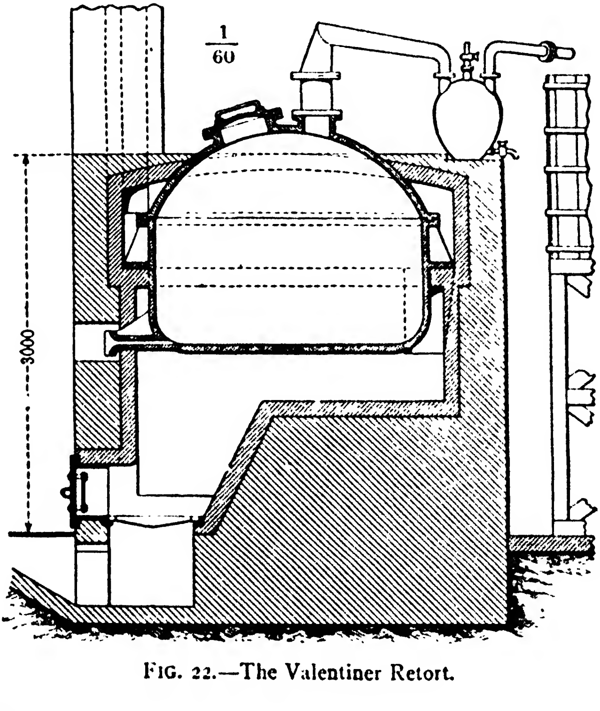

FIG. 22.—The Valentiner Retort.

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[1] B.P. 134,406, 9th Dec. 1918.

false bottom to bed itself into when coming to rest on the two faces. When in position it was packed all round with rust jointing material (p. 127) which was well caulked home. Over this rust joint a layer of " Nori " acid-proof cement was spread.

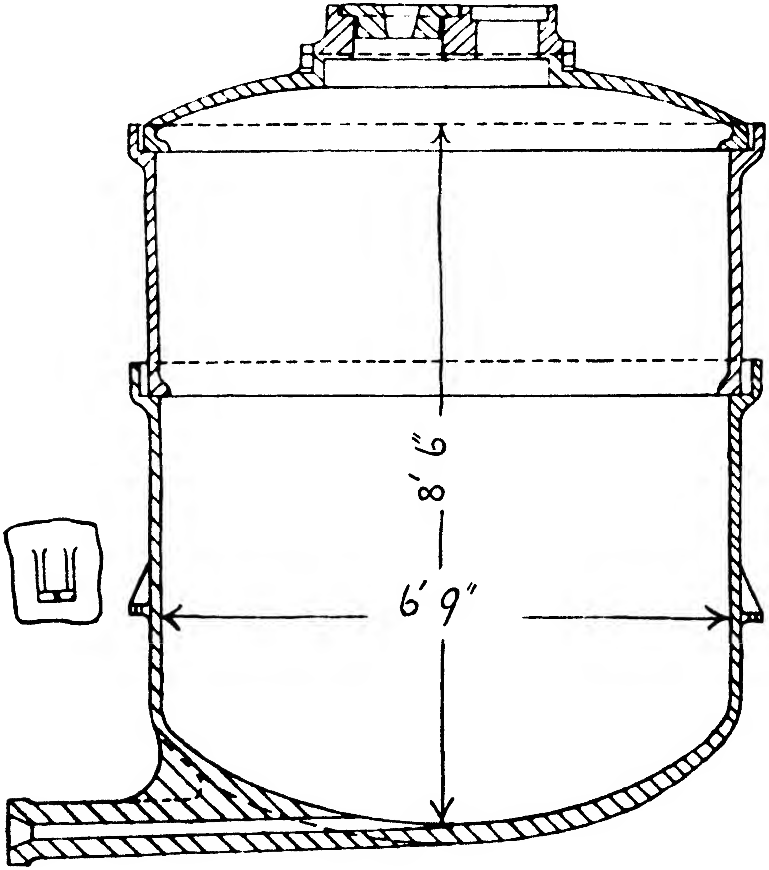

FIG. 23.—The Waltham Retort.

The only retort of this type tried at Gretna had worked thirty charges at the time the factory was closed down.

Size.

Retorts of capacities from a few cwts. to 4 tons of nitre with the necessary accompanying quantities of sulphuric acid are in use. It is highly desirable to provide ample capacity in a retort, so that during the reaction there is plenty of accommodation for the contents, which on occasions are subject to rapid and considerable increases of bulk. A pot of approx. 200 cub. ft. capacity was originally provided to work a 2-ton charge of nitrate. In practice this pot proved rather too small, especially for intensive working, and its capacity was increased to about 350 cub. ft. by the addition of a 3-ft. extension ring. This extended retort proved very satisfactory in use, and such retorts worked many thousands of 2-ton charges of nitrate during the recent war. The dimensions of this retort are given in Fig. 23.

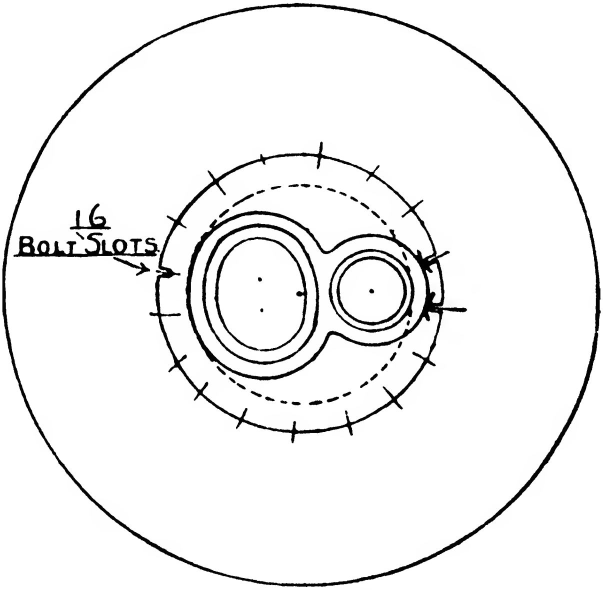

FIG. 23A.—Plan of Waltham Retort.

The Extension Ring.

The practice of using an extension ring facilitates the handling of the retort and is economical in material, since when a retort fails in use the failure is almost invariably at the bottom and the extension ring is found to be still quite serviceable.

Material.

Cast iron is universally used for nitric acid retorts, and if the cast iron is of a suitable nature it is admirable for the purpose. Although the question of providing a good acid-resisting cast iron has been acknowledged as important for many years, until recently very little systematic investigation of the subject had been carried out, with a view to defining exactly the composition of metal which will best serve under conditions met with in nitric acid retorting.

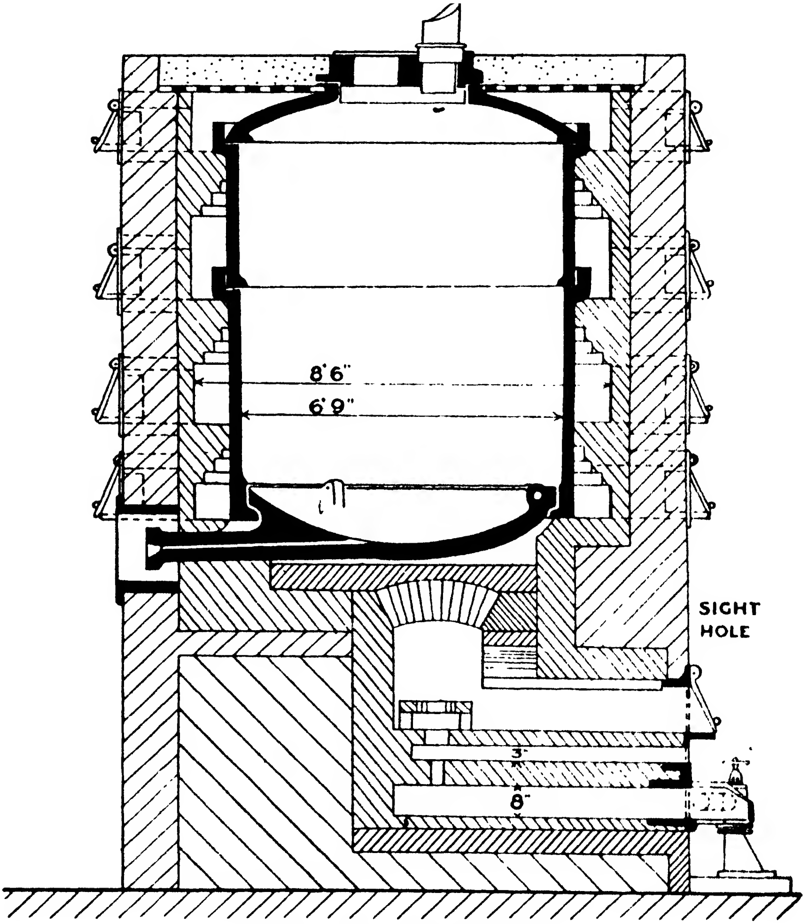

FIG. 24.—Retort with False Bottom.

Cracking and Corrosion.

It has long been acknowledged that for resistance to acid corrosion a white cast iron is most suitable, but owing to its brittle character such an iron was not considered suitable for rough usage, and a tough, strong, grey cast iron was the desideratum of the engineer and founder. To meet the needs of those working with acids, a mixed or mottled cast iron came to be used as a means of partially meeting both requirements of mechanical strength and of resistance to acid attack. Later, a grey cast iron was face-hardened where it was to be subjected to the action of acids, but vessels so prepared were not satisfactory, and this method never became general.

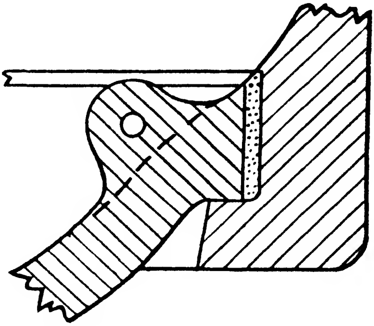

FIG. 24A.—Detail of Attachment of False Bottom.

Recent metallographical investigations of cast irons subjected to nitric retort practice confirm the long-held view as regards suitable type of metal to resist acid corrosion, but go further in showing where corrosion takes place, and why. It remains to be seen whether or not it will be possible yet to specify metal composition and details of foundry practice which will ensure the production of a uniformly good retort for nitric acid practice.

In order to ensure a good quality metal where most required, at the bottom of the retort, it would seem better for the casting to be done with the bottom downwards, so that slag intrusions of lighter density might rise clear of the bottom. This is the usual method.

In this connection, however, it must be borne in mind that the brittle phosphide eutectic has a very low melting-point, and during solidification of the casting it has a tendency to sink to the bottom, and there form points of weakness. It is desirable, therefore, that the phosphorus content of the metal should be as low as possible.

In a paper read before the Manchester Section of the

Society of Chemical Industry in February 1918,[1] E. L. Rhead considered the effect of the composition, character, and condition of the metal in cast iron upon its predisposition for corrosion under conditions of use in chemical plant. He drew attention to the fact that the ultimate analysis of cast iron, as usually stated, gives a very imperfect indication of the purity of the metal. A typical analysis of an ordinary casting is as follows: Total carbon, 3·3 per cent.; combined carbon, 0·6 per cent; manganese, 0·6 per cent.; phosphorus, 1·0 per cent.; sulphur, 0·2 per cent.; and silicon, 1·8 per cent., making a total percentage of impurities of 7·5. This figure is not a true representation of the case. Carbon is present as carbide, Fe_3C, as well as graphite; silicon as silicide; phosphorus as phosphide; and sulphur as sulphide. Reckoned as the compounds, the normal impurities in cast iron total to something like 25 cent. of the material instead of 7·5 per cent. as indicated by the above analysis. When the metal cools from fusion its ultimate character depends on the behaviour of these compounds, and not on the elements. At the casting temperature all are in solution and uniformly diffused. During cooling, as the solubility falls, one or other may separate or concentrate in the still fluid portion. The carbide under certain conditions may decompose to form graphite, the size of the flakes of which being dependent on the time occupied in the growth. The other compounds do not decompose. The portion last remaining fluid retains practically the whole of the phosphorus, and has a very low melting-point.

In the solidification of castings the liquid portion subsides by gravity into the lower parts of the casting, so long as a clear way exists and produces cavities. Any isolated portion will, as far as possible, do the same. Pressure exerted by the contraction of the solidified part may squeeze the fluid and cause it to mould itself on the existing solid portion, or even into cavities as pellets. These eutectic enclosures are commonly associated with cavities and crevices, which communicate and afford an easy path into the mass. Variation of temperature and other changing conditions will help to reduce cohesion in such a heterogeneous mass. This occurs especially at the surfaces of the graphite flakes, and the larger these are, the

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[1] *Chem. Trade J.*, 9th February 1918, p. 111.

more readily this occurs. Thus corroding liquids and gases find their way into the mass and attack the material.

In the attack of chemical vessels it was shown that actual corrosion had occurred on each side of the graphite flakes, the corroded material lying on each side of the flake. Cavities in association with the phosphide eutectic yielded on exposure an efflorescence of iron salts in patches all over the fractured surface. Reference was made to the very rapid failure of nitration pans, after having been long in use, when subjected, to more drastic treatment. It was shown that this was due to the surface having been removed by solution, exposing the more open and more highly phosphoric metal in the centre of the casting. Specimens and analyses showing these differences were given. The ultimate cracking was said to be due to the bursting pressure produced by the increase in volume due to corrosion.

In the case of high silicon alloys used for chemical vessels, it was pointed out that the same conclusions held good. Graphite should be absent, and phosphorus at a minimum. Examples showing the presence of both were exhibited, and it was shown by analysis that when acted on by acids the phosphide was preferentially attacked.

Hay and Sissons, as a result of experimental work on acids plant at H.M. Factory, Gretna, came to the following conclusions regarding the corrosion of cast iron by mixed acid of the composition H_2SO_4, 61 ; HNO_3, 20; H_2O, 19 (acid distilled in cast-iron stills):—

(1) The occurrence of graphite in the cast iron is the chief cause of this corrosion. Where the graphite planes are large and closely packed together, corrosion proceeds most rapidly.

The reasons for weakness due to the presence of this carbon would probably be:—The graphite planes prevent a proper development and interlacing of the crystals; they also furnish an entrance into the metal for the acids; the swelling of these planes would call into play a certain disruptive force; the ferrite associated with the graphite is the softest constituent of the cast iron.

(2) The phosphide areas stand up well and, as regards corrosion, the presence of the phosphide eutectic is not a source of weakness to acid attack by mixed acid of the above composition.

Analysis of the cast iron showed variations in graphitic carbon content from 1·26 per cent. to 3·46 per cent., while specimens of stills from the same foundry showed marked differences.

Note.—The particular investigation here considered refers to corrosion of the stills used in distilling nitro-cotton spent acid (see p. 179). These stills failed owing to distinct solution of metal causing local holing, and not as a result of cracking.

In regard to strength of the retort and general capability to withstand the stresses and strains to which it is subjected in alternate contractions and expansions, a view now held is that the bottom of the retort ought to be modelled on the catenary curve. Investigation in this direction is left to normal works experience, and here so many factors come into play that clearly defined results are difficult to deduce. The author's experience in intensive nitric retort practice tends to the view that a flat-bottomed retort is not desirable. When a retort fails in use it is almost invariably found that the failure is due to cracking, and the possibility is that corrosion and stress and strain effects are together responsible for the failure. E. L. Rhead[1] attributes the cracking of cast-iron nitrating vessels attacked by acids to the bursting pressure produced by the increase in volume due to corrosion.

The author's experience has been gained mainly during the years of the war, when nitric acid production was so urgent that very rapid working had to be developed, and the retorts were subjected to abnormal sudden heatings and coolings. With normal working, when reasonable heating up and cooling down periods can be given, the modern nitric acid retort will undoubtedly have a very long life. It seems desirable, however, that best specifications for foundry practice should be developed and laid down to ensure as far as possible general satisfaction.

[1] *Vide supra.*

RETORT SETTINGS.

Supporting the Retort.

A nitric acid retort should be firmly supported in its setting, with ample freedom for expansion and contraction. The ideal way of supporting a retort would appear to be to hang it in the flue of the fire, but this arrangement is not quite practicable.

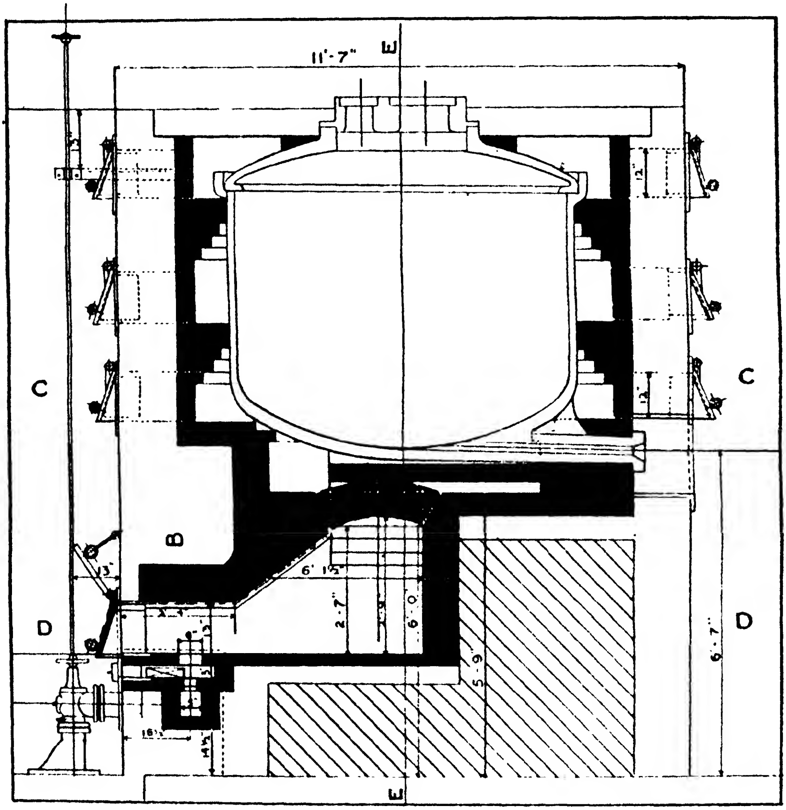

FIG. 25.—Unsuitable Support.

An approach to the ideal is to build firmly in the setting steel girder brackets to carry the lugs which are cast on the retort, and then to ensure that brickwork is not built anywhere to resist freedom of expansion and contraction of the metal, In this connection note should be made that the run-off pipe at the bottom of the retort must not be held tightly in a mass of brickwork.

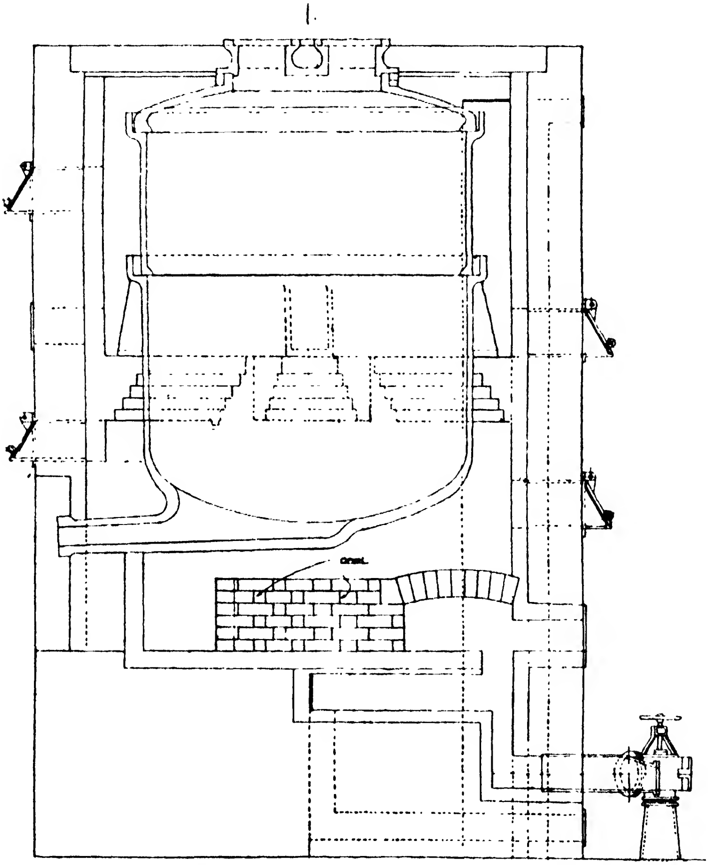

FIG. 26.—Suitable Support (H. S. Denny).

Figs. 25 and 26 show respectively unsuitable and suitable methods of supporting a retort. In Fig. 25 note:—(1) Mass of brickwork under retort; (2) slender support at bottom near circumference; and (3) how the nitric cake run-off pipe is embedded in brickwork.

Flues.

It is usual practice to circulate the hot gases from the fire several times round the retort before discharging them from

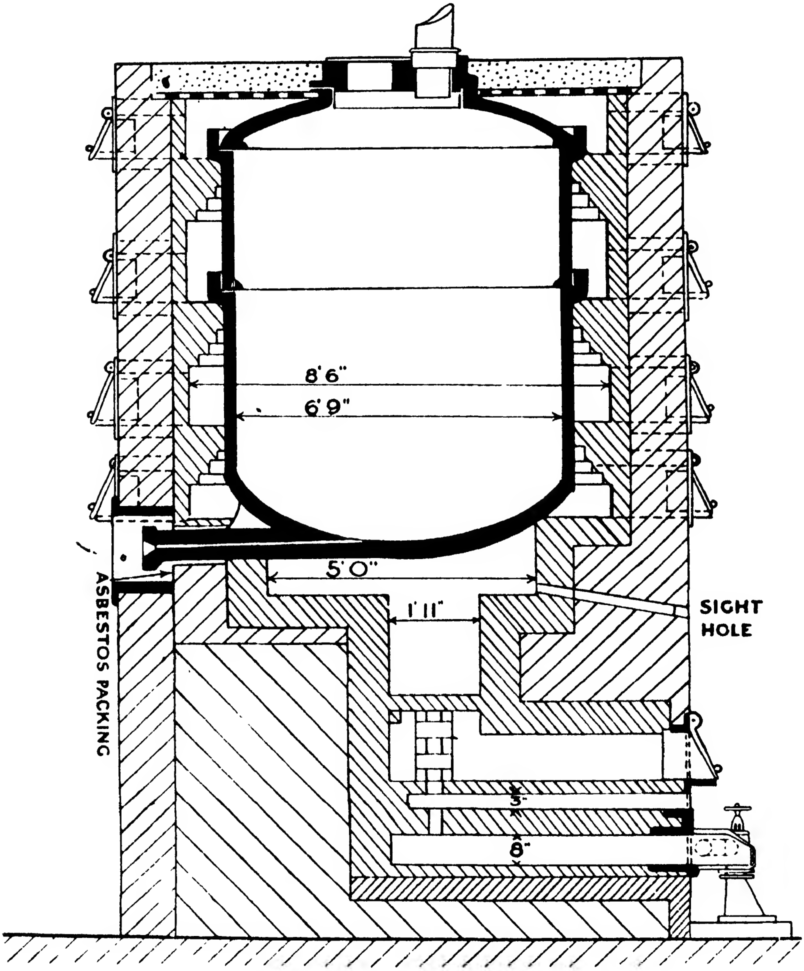

FIG 27.—Retort Setting, H.M. Factory, Gretna.

near the top of the setting to the waste gas flue en route for the chimney. Successive flues have their inlets and outlets at opposite sides of the setting, and in this way it is ensured that the retort is evenly heated. The main lid of the retort is within the last flue, and this ensures the maintenance here of a temperature sufficiently high to avoid condensation of nitric acid within the retort, and thus prevents nitric acid corrosion.

Fig. 27 shows a setting with four horizontal circular flues. The downtake flue carrying waste gases to the chimney should be provided with a slide damper.

If gas or oil fired, the flues should be provided with a number of easily lifted explosion doors to safeguard the structure in the case of explosion.

Combustion Chamber.

This naturally depends on the source of heat. Generally speaking, it is bigger for gas or oil firing than for coal or coke. In any case, provision should be made for supplying enough air for complete combustion. First class fire brick should be used in the construction, and they should be well laid by experienced men. In gas and oil firing, opinions are divided whether or not to provide in the combustion chamber some system of chequer brickwork to assist in complete combustion.

Complete Structure.

For stability and conservation of heat, the structure carrying a nitric acid retort and its flues must be substantially built with containing walls up to 18 in. thick. Where more than one retort is built, several may be contained within the same external walls. Generally the plan is rectangular but individual settings may be circular.

The brickwork, if substantially built, does not require stays, though these are often provided to give additional support.

CONDENSING SYSTEMS.

Early Types.

Formerly in the manufacture of nitric acid, only air condensation, usually in Woulff's bottles, was provided, but now both air and water cooling are made use of. The following diagrams (Figs. 29, 30, 31) of early nitric acid condensing systems are from a paper by Guttmann.[1]

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[1] *J. Soc. Chem. Ind.*, 1893, **12**, 203-16.

Requirements.

Many devices have been introduced for bringing about the cooling of nitric acid vapours and each system in use has certain merits and claims a certain measure of support. For success as a large scale nitric acid condenser, the apparatus employed must answer a number of requirements, the most important of which are detailed overleaf, viz. :—

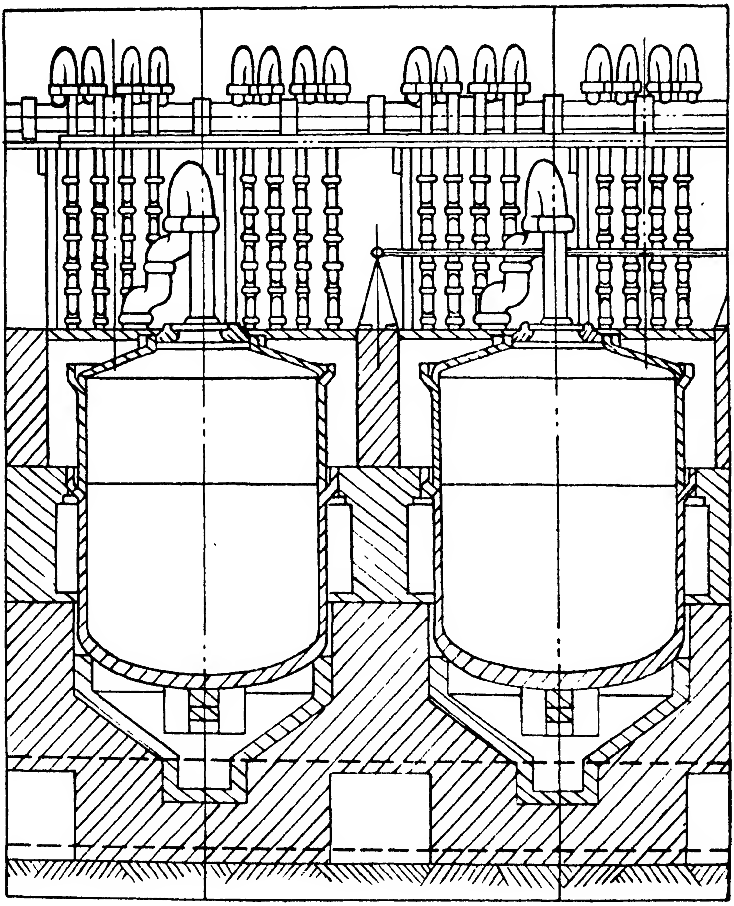

FIG. 28.—Retorts in Settings, H.M. Factory, Greetland.

1. The materials of construction must:—

(*a*) Withstand the corrosive action of nitric acid.

(*b*) Not be porous.

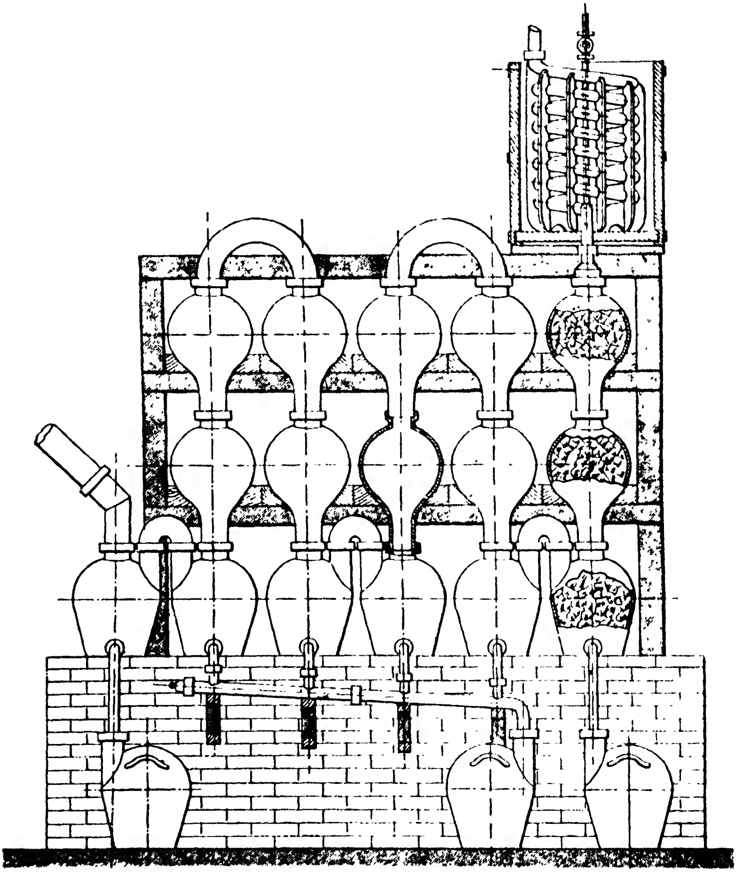

FIG. 29.—Early Condensers.

(*c*) Withstand rapid temperature changes and a high temperature gradient without cracking.

(*d*) Stand normal plant handling.

(*e*) Have as high a thermal conductivity as possible to ensure rapid heat exchange and efficiency of condensation.

2. The apparatus must be simple in construction and all parts should be readily accessible for adjustment or repair.

Divisions.

Although each distinct type of plant may vary in detail, the general lines of treatment of a modern nitric acid condensing system are indicated in the accompanying diagram, Fig. 32, from which it is seen that there are five principal divisions, viz., conduit pipes to condenser proper, condenser proper, fume main, acid mains, and acid receivers.

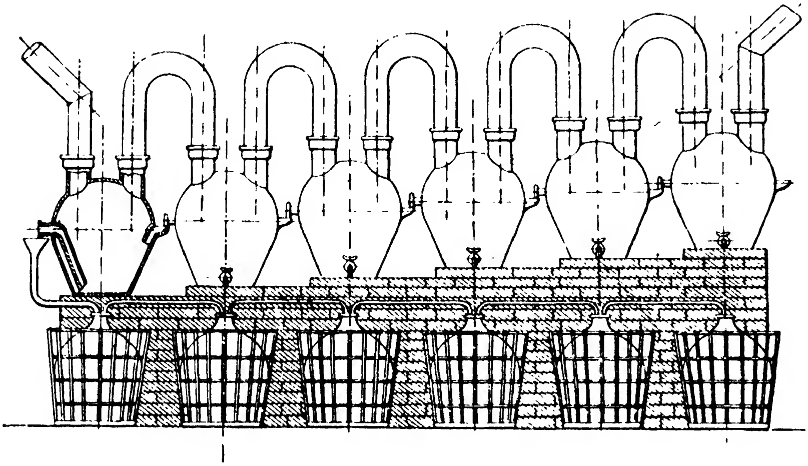

FIG. 30.—Early Condensers.

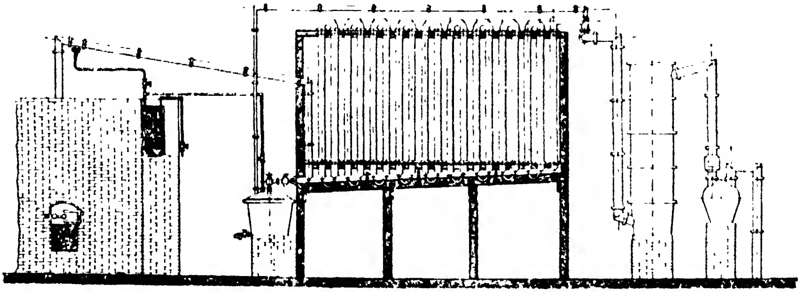

FIG. 31.—Early Guttmann Condensing System.

It is not designed in what follows to exhaust the types of condensing systems employed, but a number of successfully used apparatus will be considered.

In order to cope satisfactorily with the rapid evolution of nitric acid vapours from the retort at the period of distillation known as the "reaction," the condensing system should have ample capacity (at this period, the evolution of vapour and hence the volume to be dealt with in the condenser, may be many times the average evolution over the whole distillation period), should be as efficient as possible, and should give freedom for passage of uncondensed gases. In the air-cooled portion of the apparatus, before rapid condensation is effected, there should be easy passage for the gases with as few changes of direction as possible. (Air cooling, as such, is now practically obsolete, but the hot gases are carried a certain distance from the retort to the water-cooled condensing apparatus in pipes which are only air-cooled. This pipe system is here represented as the air-cooled portion of the condensing system.)

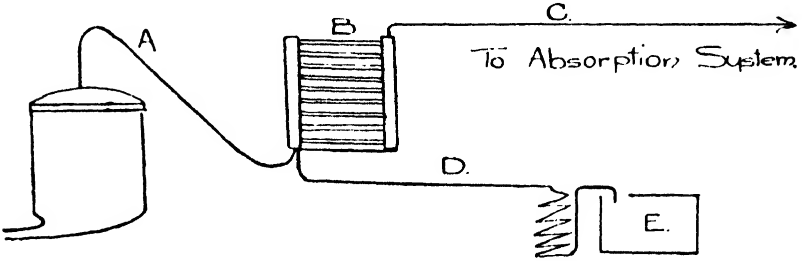

FIG. 32.—Diagrammatic Representation of Condensing System.

A. Conduit Pipes to Condenser Proper (air cooling).
B. Condenser Proper (air and water cooling).
C. Uncondensed Fume Main (leading to absorption system)
D. Acid Mains. E. Acid Receiver.

Conduit Pipes to Condenser.

The full volume of distilled gases is present here, and ample capacity to carry even explosive-like discharges should be provided. The provision of an easy flow is much to be desired, and abrupt and awkward bends should be avoided. The simplest and most satisfactory system of delivery is obtained by the use of simple spigot and socket pipes to give a conduit as shown in Fig 33.

By the use of the S pipe to give a cascade conduit as shown in Fig. 34, special point is made of the horizontal joints. However, the joints in the simple pipe conduit system shown in Fig. 33, can be well made, are not subject to much danger from acid contact, and have been proved to be lasting. In the simple system the gas flow is easier, and there is the decided advantage that if a pipe cracks on the under side, it can be turned with the crack upwards and patched, whereas the pipe unit in the cascade system (a much more costly one) has to be discarded if cracked.

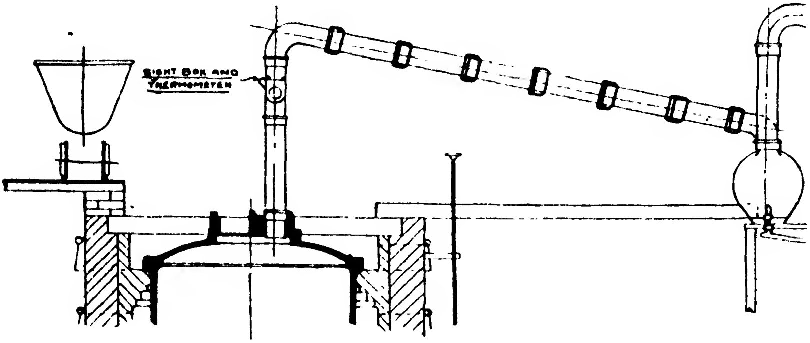

Fig. 33.—Straight Pipe System.

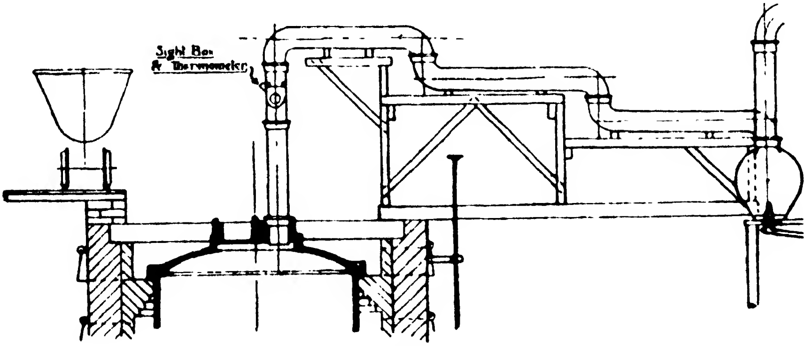

Fig. 34.—Cascade System.

It is now fairly general practice to allow only a short uptake from the retort before bending over towards the condenser proper, and it is no doubt better practice to get the gases away for condensation thus than to hope for some reflux purification in a tall uptake pipe.

Distillation temperatures are attained rapidly, and it is

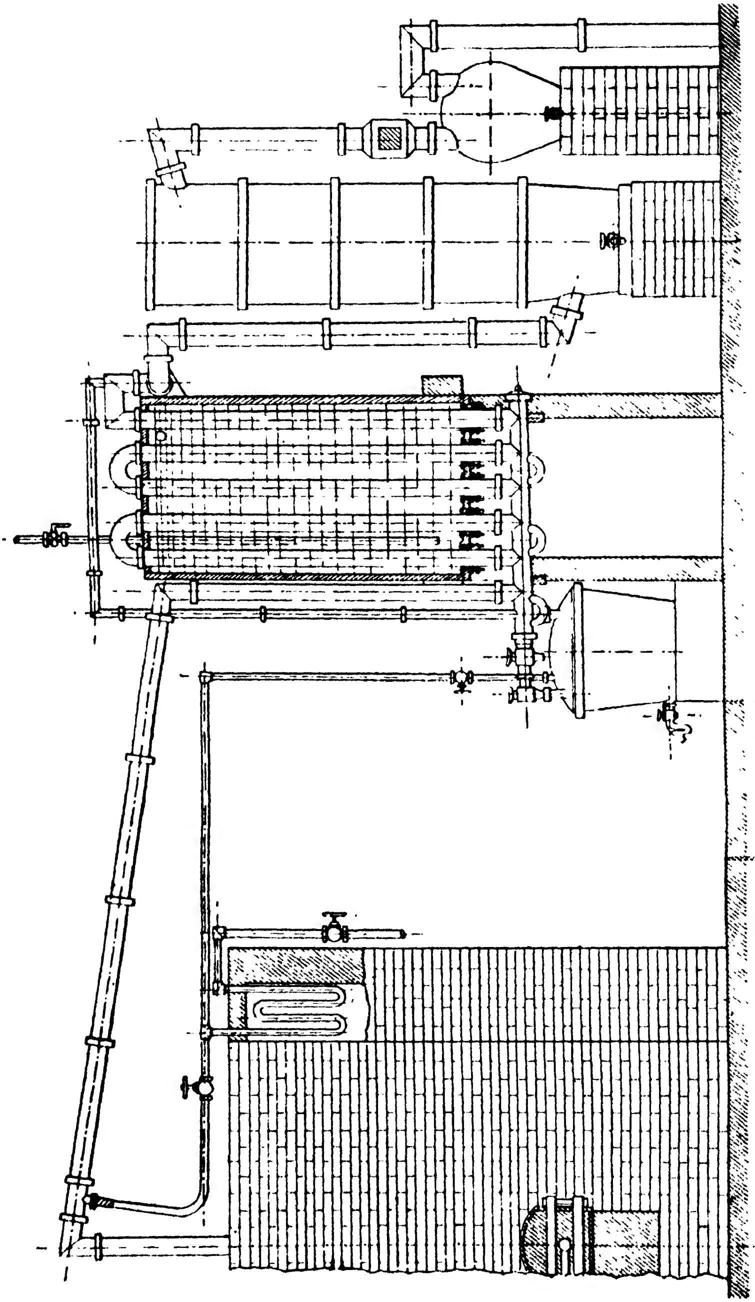

FIG. 35.—Water Cooled Guttmann Condenser.

important to have the first pipe system of material which will withstand the conditions prevailing during distillation. Silicon iron is certainly the best material for this purpose. The pipes should be comfortably yet firmly supported on wood runners which are so spaced that work such as rejointing of pipes can be done easily.

Types of Condensers.

Guttmann.—Oscar Guttmann was a pioneer in large scale nitric acid plant, and his condensing system has been very largely used. In the early days Guttmann relied on air cooling, but later, on introducing water cooling, he was able to cut down his condensing area to one quarter. Guttmann's apparatus consists of perpendicular pipes with acid lutes leading to common collecting channel pipes, and his earliest water-cooled apparatus is illustrated in Fig. 35.[1]

Modern adjustments of the Guttmann condenser have been mainly concerned with simplifying the design to make it more acceptable as a works plant. Fig. 36 shows a Guttmann type condenser of " Ironac " metal.

I am indebted to Mr B. Burrow, who has had extensive experience of the Guttmann condenser alongside the Waltham coil and the S-pipe at the works of Messrs Chance & Hunt, Oldbury, and at H.M. Factory, Greetland, for the following information regarding its use. With easy conditions of working (24-hour cycle), and preferably distilling nitrate with 80 per cent. H_2SO_4, good results, both as regards efficiency of process and quality of product, were obtainable when the earthenware was very good. If, however, the earthenware pieces did not prove to be good, much trouble ensued, as dismantling and reassembling could not easily and expeditiously be carried out. Under hurried conditions of working, pipe breakage was excessive and general maintenance charges were high. Inability to detect acid leakages during working led to much acid dilution and wastage of acid and plant. Consequent dismantling of the pipe system led to further breakage because of the somewhat unwieldy character of the pipes. Comparatively small bore outlets from the

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[1] *J. Soc. Chem. Ind.*, 31st March 1893.

Y-pieces feeding acid to the collecting channels led to choking and consequent difficulties. The large number of joints was also a source of continual trouble. Generally speaking, the condenser is not sufficiently flexible. Even under the most favourable conditions the working costs with the Guttmann condenser are high, and in comparison with the silica coil

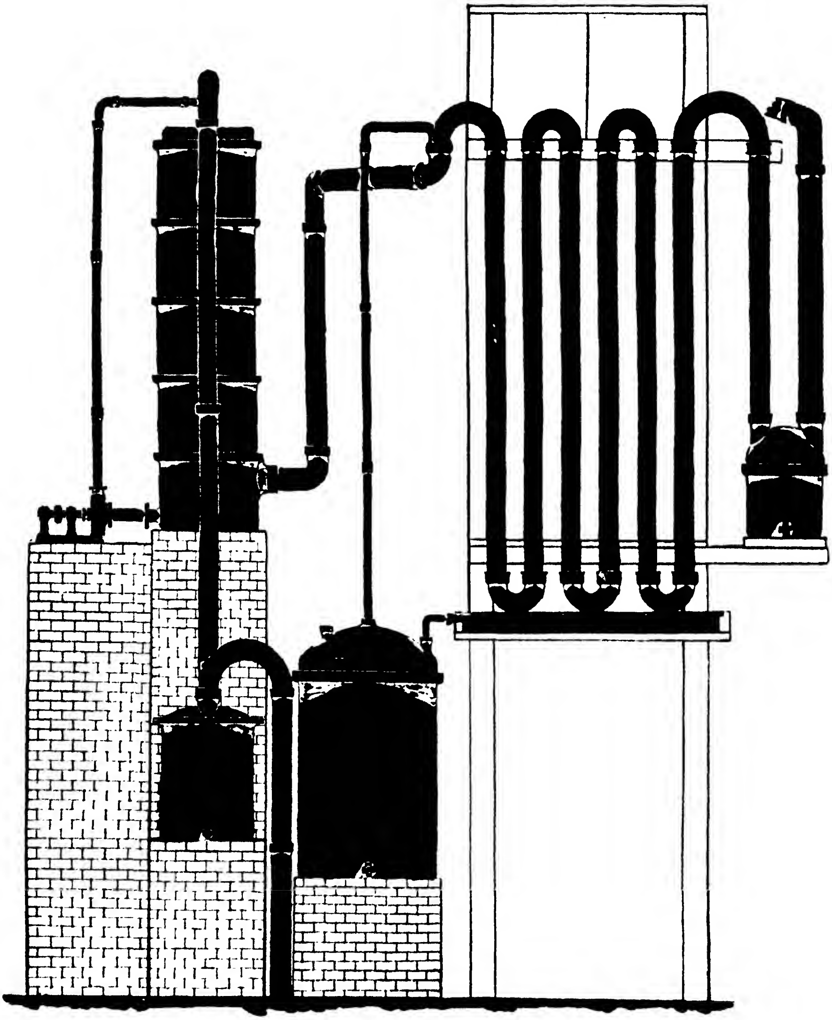

FIG. 36.—"Ironac" Condenser (Guttmann Type).

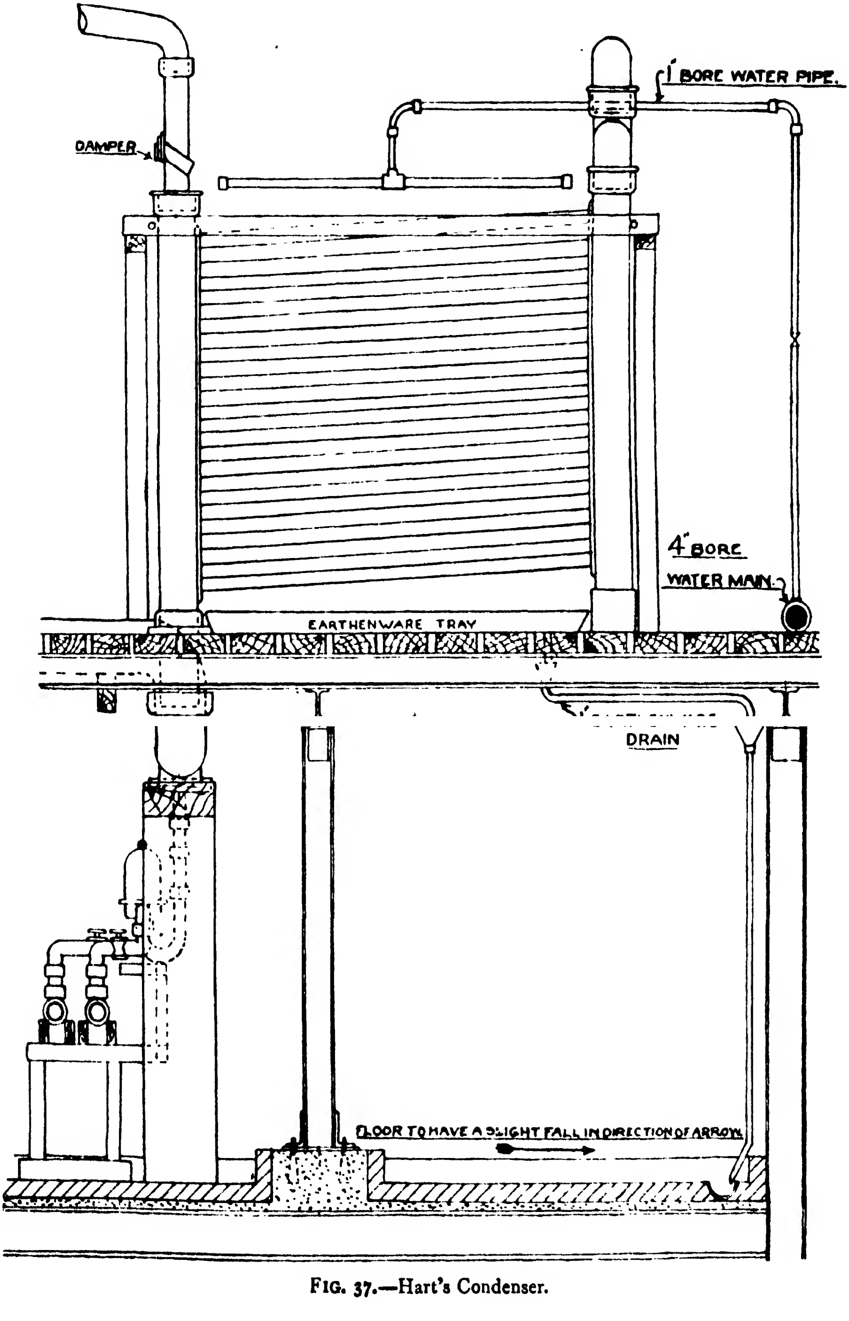

FIG. 37.—Hart's Condenser.

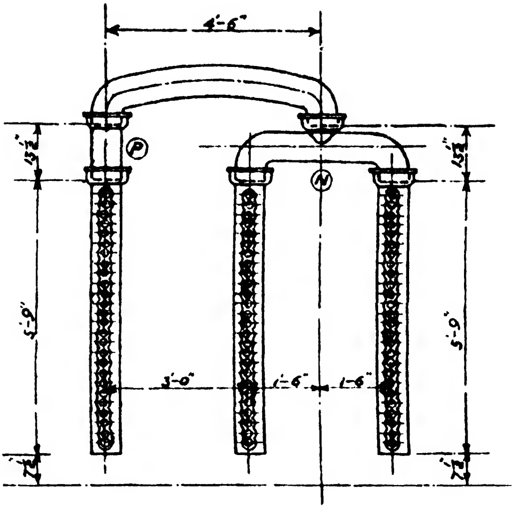

FIG. 38.—Back Standards (Hart's Condenser).

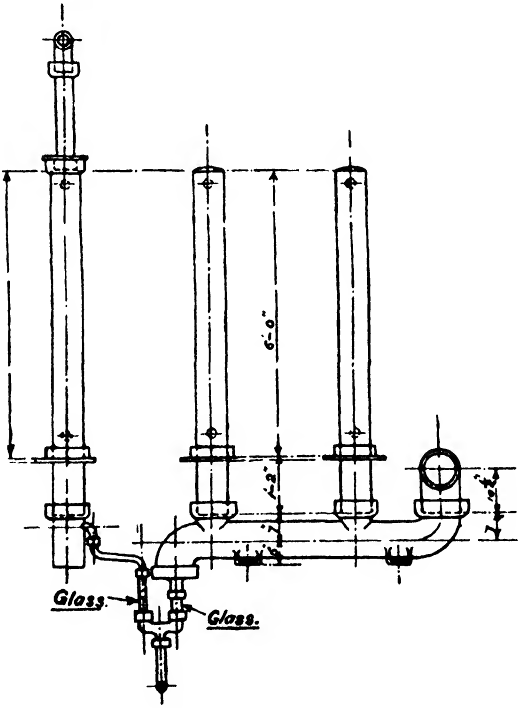

FIG. 38A.—Double Entry S-Bend and Front Standards (Hart's Condenser).

and S-type plants the Guttmann plant has little to recommend it.[1]

Hart.—Dr Edward Hart was one of the pioneers of large scale distillation of nitric acid in America, and early sought a condensing system which should approximate somewhat to the Liebig condenser so successfully used in laboratory practice.

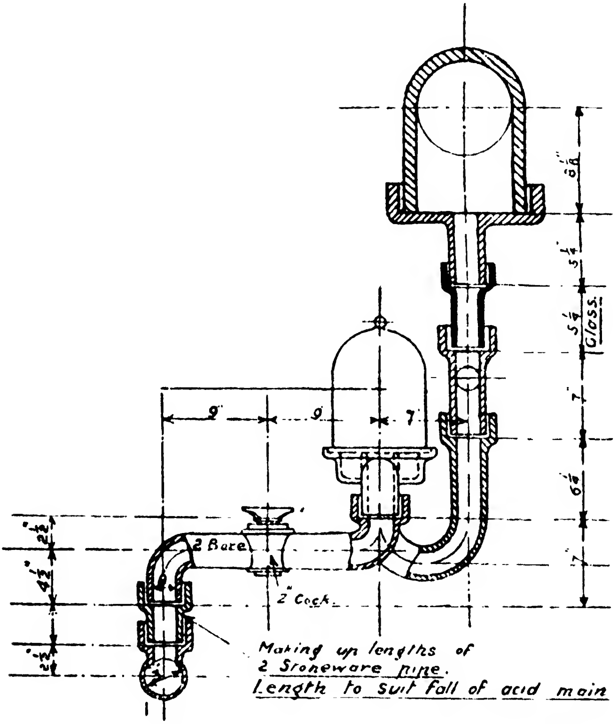

FIG. 39.—Acid Delivery from S-Bend to Acid Main *via* Still Watcher (Hart's Condenser).

As finally developed, the Hart condenser consists essentially of wide vertical pipes (standards) of pottery or silicon iron, which are perforated to allow the introduction of a number of connecting glass tubes fitting nearly horizontal. As the nitric acid vapour passes into the standards it is split up into a number of small streams. Water is allowed to drip over the glass tubes and efficient condensation is effected.

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[1] Silica ware has been used for the Guttmann plant, but though its use has given increased reliability it has not increased its flexibility.

Many modifications have been introduced in regard to details of gas conduits and acid run offs, but the actual condenser units remain practically unaltered. A modern type of Hart condensing system leads the gases from the retort by suitable pipes to a double entry S-bend pipe, which carries the two front standards of two condenser units arranged in parallel.

Entering these two standards the gases split up and pass across by the glass tubes to the corresponding back standards, from the tops of which they are gathered by a breeches pipe into a U-pipe leading to the back standard of a third condenser unit. From here the gases pass to the corresponding front standard, from the top of which they pass to a fume main leading to an absorption system.

Condensed acid flows down the slightly inclined glass tubes, down the standards and into the S-pipe, from which it is delivered by a socket delivery connection via a "Still Watcher" to suitable receivers or to acid mains. Condensed acid from the third Hart unit flows down the back standard and socket delivery pipe to meet that coming from the S-pipe.

An earlier design using the Hart system provides large Woulff's bottles as gas and acid receivers before the condensing sets, and the third condensing set receiving its supply of gases from the bottom by the back standard, is constructed differently from the first two sets in parallel.

In the middle of the back standard is a baffle having only a small drip hole. The gases thus rise half way up the back standard and across to the front standard, from the top half of which they pass across to the top half of the back standard, and from the top of this the uncondensed gases pass to a fume main as before.

This type of third condenser allows much less nitric acid vapour to pass forward into the uncondensed fume main, but tends to prevent freedom of gas flow.

American practice has developed a Hart condenser with 3-in. glass tubes in place of the 1¼-in. tubes common in English practice. The standards are generally provided with baffles so that 5 tubes are first used leading from front to back, then 4 tubes from back to front, and 3 tubes front to back again. Two condensers are used in series and a third one takes the uncondensed gases from two retorts. Condensation thus takes

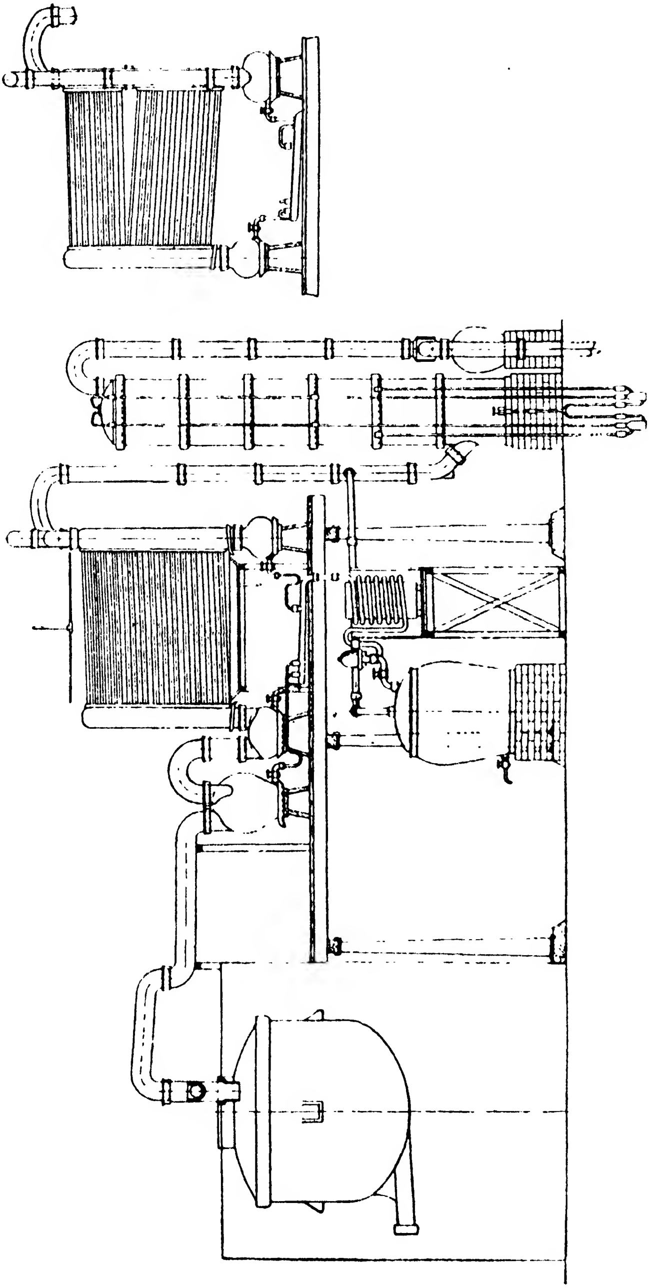

FIG. 40.—Hart's Condenser (Early Design).

place in 30 glass tubes per retort instead of 78 as in English practice with the same condensing surface. This effects a considerable reduction of joints, but the heat exchange can not be so good owing to the reduced velocity of the gases.

The glass tubes are usually covered with a coarse cotton cloth to get an even distribution of water over them. The cloth may be torn into strips about 4 in. wide and interwoven with the tubes, round one tube to the right, then to the next tube to the left and so on, the strips being kept 4 to 6 in. away from the standards. Rubber rings are useful on the glass tubes at their lower ends to prevent water running on to the joints where the glass tubes enter the standards. Water from the condenser is collected in stoneware trays and led to waste by stoneware down pipes.

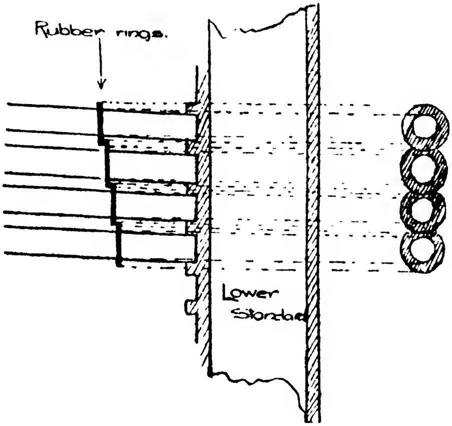

FIG. 41.—To show the Use of Rubber Rings in preventing Cooling Water reaching the Joints where the Glass Tubes enter the Standard.

CONDENSER JOINTS.—In a plant handling charges of 2 tons of nitrate of soda, the three banks of glass tubes in the Hart condenser necessitate 156 acid and gas proof joints, and the greatest care is necessary in selecting jointing material. In fixing the glass tubes, they are placed in position in the sockets provided in the standards and the joints are made in the following manner. A ring of blue asbestos cord is first put in. A layer of soft putty (p. 127) is then inserted and pushed gently against the cord with a suitably shaped wood tool. Another ring of cord follows and then another layer of putty. Over this is put a facing of asbestos and silicate cement (p. 127). When this is firmly set, the surface of the joints is painted over with tar. Such joints will stand normal wear for a considerable time. However, sudden pressures in the retort, and sudden rushes of gas, must be avoided if the joints are to have a long life.

The Hart condenser is too intricate, there being far too many pieces jointed together. As a result, the labour required to watch it is considerable, and the cost of repair and general upkeep make it expensive to maintain. If it is not maintained well, there is ample opportunity for dilution of condensed acid with cooling water, for leakage of acid, and for leakage of fume. These are serious disadvantages which have to be taken into account. On the other hand, the condenser gives rapid condensation, and provides an acid very free from nitrous impurity. It is an excellent condenser to watch, the glass tubes providing very clear and accurate indication of the progress of distillation.

In intensive working during 1917 the cost of upkeep of a battery of Hart's condensing sets at Gretna, producing 3051 tons of HNO_3, was £286, *i.e.*, 1s. 10d. per ton of HNO_3 produced.

Skoglund.—This condenser, now rarely met with, consists essentially of a quartz packed earthenware tower, similar to an absorption tower (p. 99), though smaller, surmounted by a coil over which water is allowed to trickle.

The hot vapours passing from the retort are mixed with air, supplied by a suitable injector, and then led into the bottom of the quartz packed tower, down which a stream of hot condensed acid flows from the condensing coil above the tower. The passage of the hot gases over the descending acid causes an efficient bleaching (see p. 172) of the latter, and the acid flowing out at the tower base is particularly free from nitrous acid and chlorine. This hot acid passes through a cooling worm before being led to storage.

Uncondensed gases escaping from the top of the condensing coil are carried forward to an absorption system.

In order to avoid breakage, the condensing tower is insulated, and it is designed as far as possible to provide continuous working in order to avoid big temperature variations. For this purpose it is made possible to use one condensing set for several retorts which can be worked in succession.

Waltham Reflux Coil. — Introduced at H.M. Factory, Waltham Abbey, this condensing system makes use of water-sprayed silica ware coils in which the nitric acid vapours pass upwards, and down which condensed acid flows to a suitable receiving system. Unconsensed gases pass from the top of the coils to fume mains. A number of coils may be worked in parallel, the gases from the retort being received into a trap or reflux box for distribution to the respective coils.

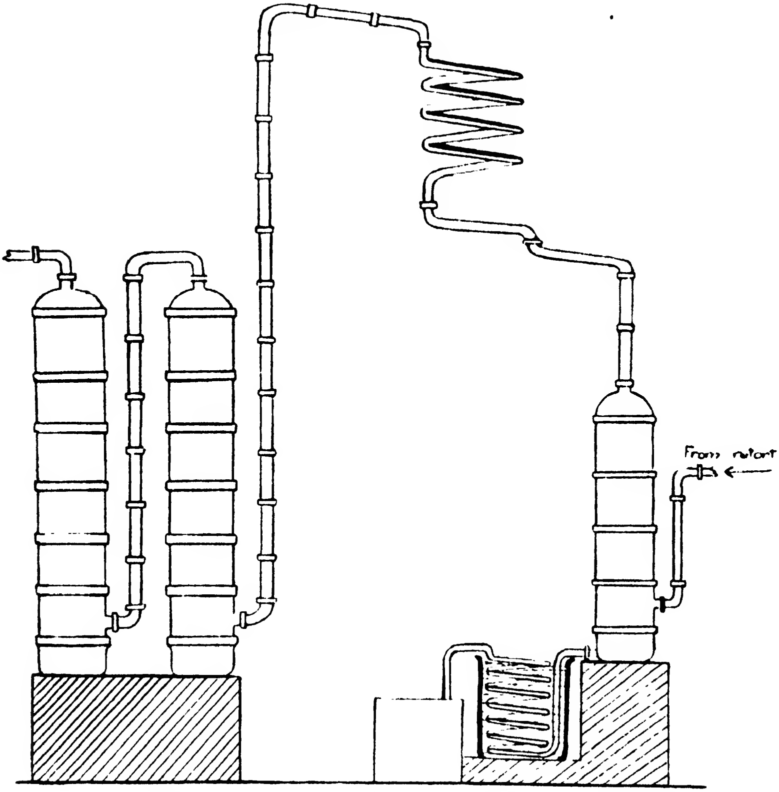

FIG. 42.—Diagrammatic Representation of the Skoglund Condenser.

This condenser is very simple in construction, but fails to give perfectly easy passage for the gases. The reflux action causes a throttling effect which leads to trouble when extra rapid gas evolution has to be coped with. With easy working of the distillation process the coil condenser works very satisfactorily. A somewhat serious disadvantage lies in the fact that the condensing unit is so large, and a crack or breakage affects the whole condenser. The number of joints in this condenser is very small, and generally speaking the maintenance requirements are light.

S-Pipe.—Several factors have led in late years to the simplification of design in nitric acid condensation plant, and largely as a result there have been evolved a number of condensing systems mainly composed of large bore pipes suitably connected and cooled. Two factors of importance in developing this type of condensing system were (1) necessity for plant to require very little attention owing to shortage of labour during the war; and (2) need to adapt plant to suit the special materials of construction, fused silica ware and acid-resisting irons, both of which provide some difficulties as regards manufacture. Generally speaking, this non-intricate, easy flow type of plant has proved very successful, and will, no doubt, soon become standardised into a fairly generally accepted system.

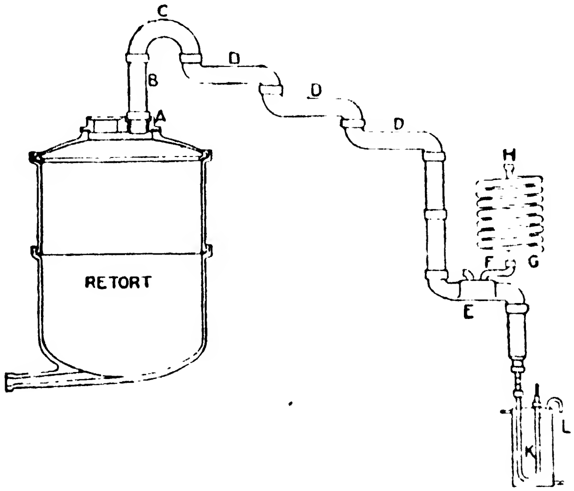

FIG. 43.—Reflux Coil Condenser.

However, where particular conditions of acid requirements exist, there may long linger a tendency to believe that this

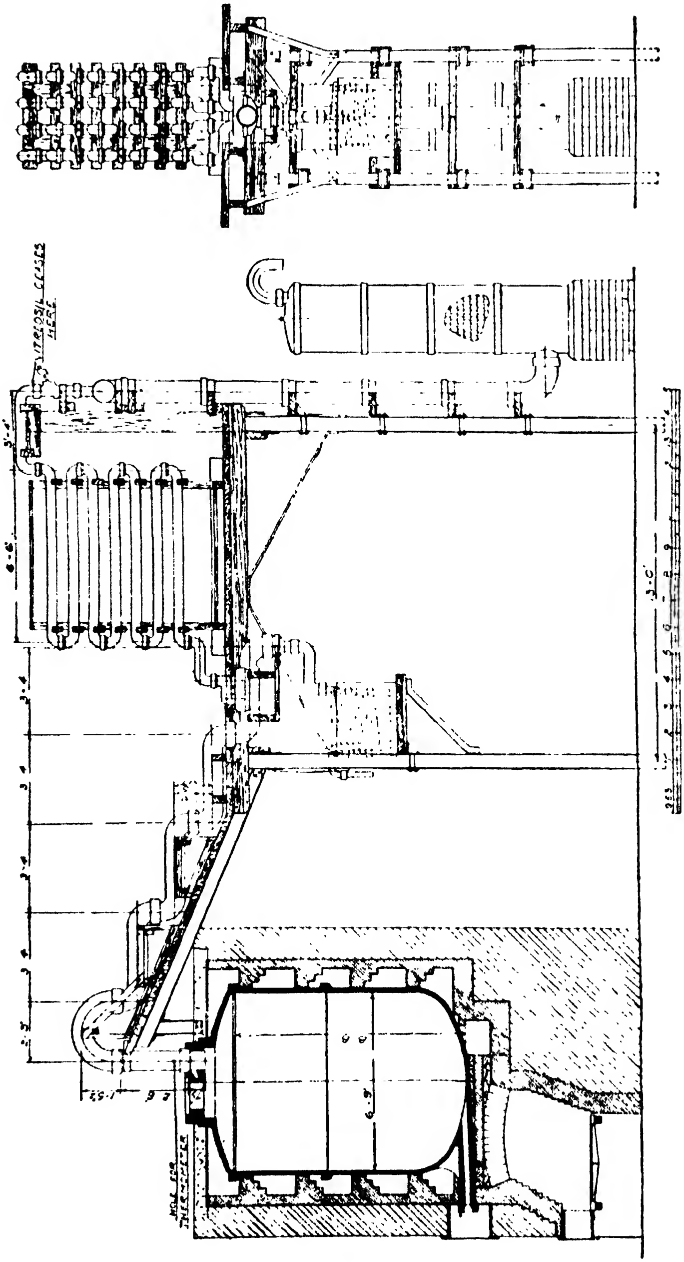

FIG. 44.—"Vitreosil" S-Pipe Condensing Plant (Thermal Syndicate).

or that system is the only one capable of providing the exact requirements.

Figs. 44 and 45 show typical S-pipe condensing systems.

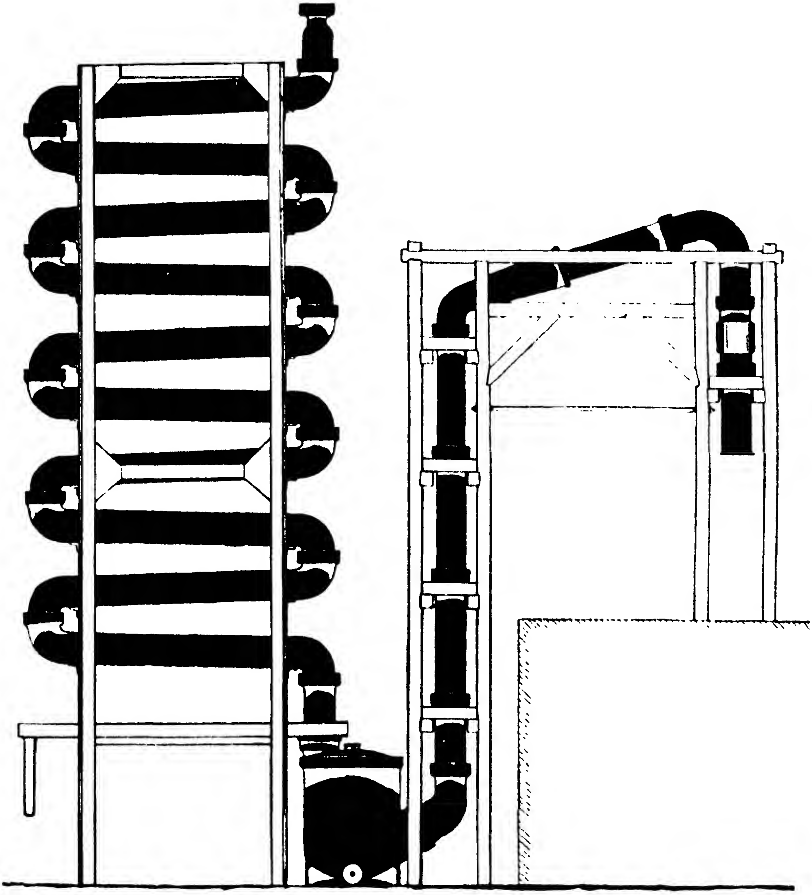

FIG. 45.—Haughton's "Ironac" S-Pipe Condenser.

The Ceratherm prism condensing plant follows the normal S-pipe type, but differs in the use of pipes of triangular section instead of the normal ones of circular section, whereby increased cooling surface is provided.

The S-pipe condenser is perhaps the simplest of condensers. It is simple in construction, readily accessible, and generally proves quite successful. This condenser readily lends itself to construction in acid-resisting metal or in silica ware. It has been found advisable to provide some packing material inside the horizontal portions of the first few pipes to avoid uncondensed nitric acid passing to the fume main. This packing may be broken silica ware or special spiral packings in acid-resisting iron. Owing to the freedom of gas passage, rapid distillation generally entails a considerable passage of nitric acid into the fume main. The total number of joints on this condenser is not excessive, and an advantage with those used is that they all lie horizontally, thus enabling tight joints to be made with considerable ease.

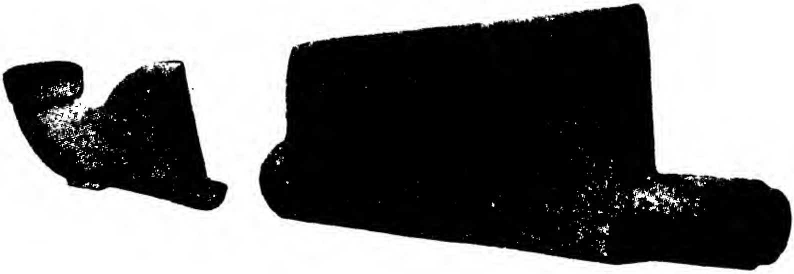

FIG. 46.—Ceratherm Prism (Patented).

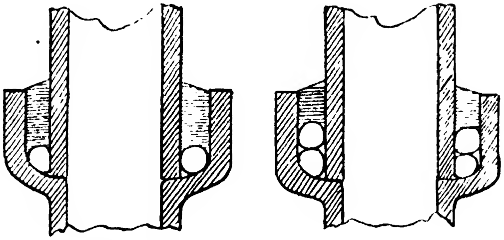

FIG. 47.—Spigot and Socket Joints.

The pipes are suitably jointed in the following way. A ring of blue asbestos rope or cord is laid in the faucet base. Above this a layer of soft putty (p. 127) is rammed in securely and faced with tar.

Hough.—This box-like condenser, named after its inventor and patentee, is very compact and effective. It was introduced in Canada, is most used in America, and is now finding favour in this country. The hot nitric acid vapours are led into rectangular boxes which carry a series of double U-pipes through which runs cooling water. The condensed acid is led off from the bottom of each condenser box. This condenser is often used to take the hottest gases, and subsequent condensation of vapours passing forward is effected in S-pipes.

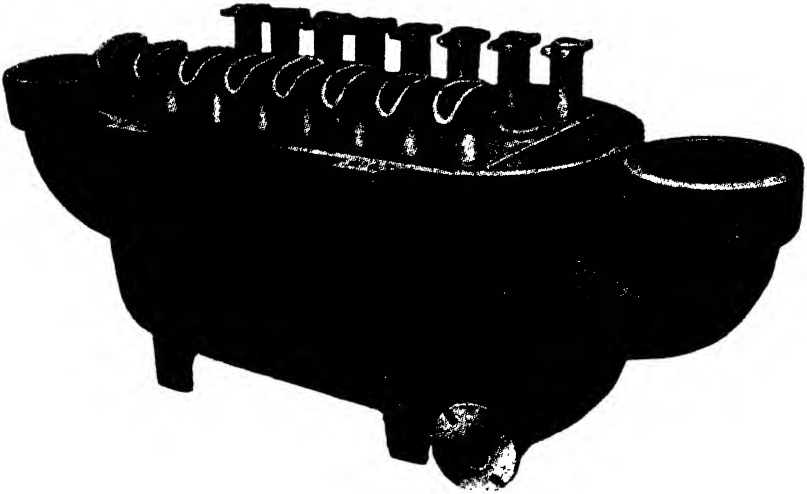

FIG. 48.—The Hough Condenser.

The condenser is usually built in acid-resisting iron, and is handy and free from joint troubles. The unit is relatively large and breakage involves the whole unit. Breakage due to freezing of the contained water is a possibility not to be overlooked.

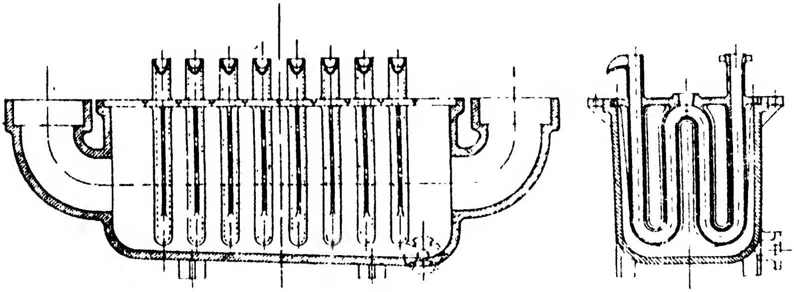

FIG. 49.—Hough Condenser in Sections.

Fig. 77, p. 135, shows an arrangement featuring the Hough

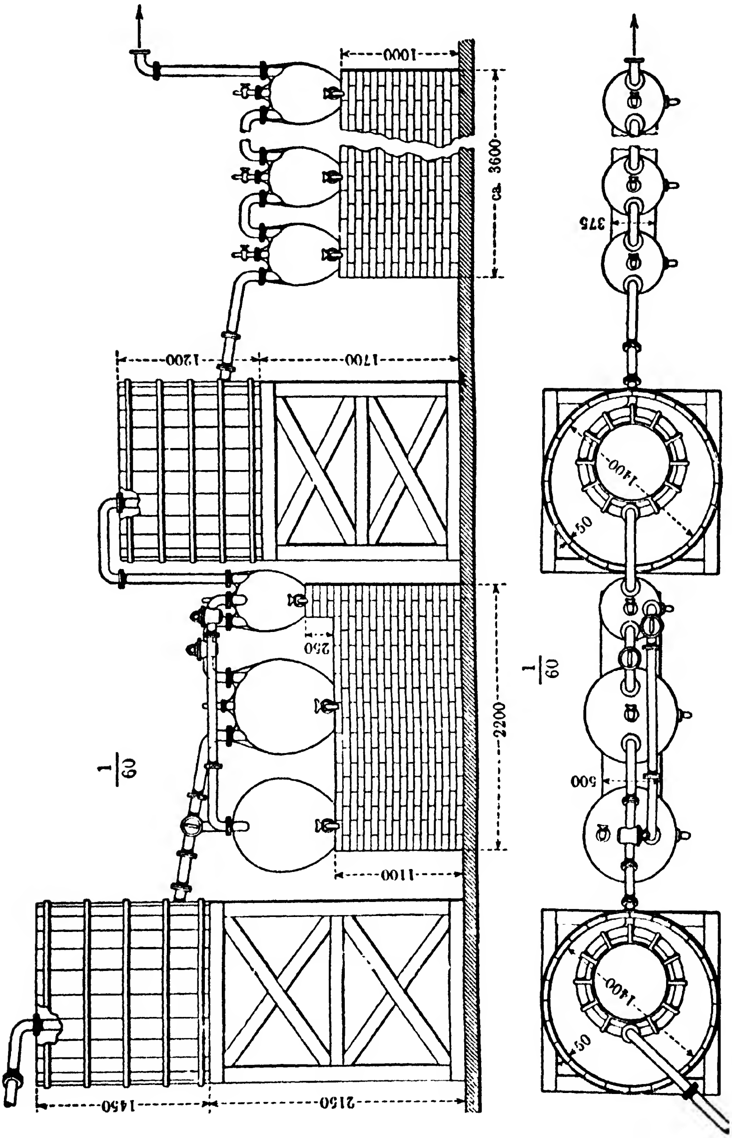

Fig. 50.—Valentiner Condensing System.

condenser, followed in turn by water-cooled silica 8-pipes and vertical air-cooled pipes.

An American practice is to use a preliminary cooling box containing only one double U-tube carrying water before leading the gases into Hough condensers set in parallel.

Valentiner.—In Valentiner's vacuum process of nitric acid distillation, condensation is effected principally in cooling coils totally immersed in water. Some condensation is also effected in air-cooled Woulff's bottles, which serve to receive the condensate. Fig. 50 is self-explanatory and shows a typical Valentiner condensation plant.

A modern Valentiner plant installed at the Huddersfield works of British Dyestuffs Corporation receives the hot gases in water-sprayed Narki S-pipe condenser sets in parallel before passing to the normal earthenware coils, also in parallel, immersed in water. In this case the usual second coil is dispensed with.

Owing to the fact that the Valentiner plant is worked under reduced pressure, it is very necessary to ensure that all joints, particularly those in contact with water, are kept sound. The number of joints is considerable, and the keeping of them in satisfactory condition entails considerable labour and time.

Well cared for, the Valentiner plant gives satisfaction.

MODIFICATIONS OF THE VALENTINER PROCESS.—During the war, Frischer, in Germany, developed a much bigger unit for the vacuum process than was used by Valentiner, and introduced a rotary liquid sealed pump in place of the relatively troublesome reciprocal pump formerly employed.

In America, Hough uses a mechanical stirring device in the retort in his vacuum process, scrubs the uncondensed vapours from the S-pipe condenser in sulphuric acid, and maintains a vacuum of about 20 inches of mercury in the system by means of a rotary sulphuric acid sealed pump. By this process it is claimed that five charges can be worked in twenty-four hours, producing acid of 91 per cent. HNO_3 with an overall recovery of 97 per cent., and a fuel consumption of only 0·075 ton of coal per ton of HNO_3 produced.

Types in Use.—Of eleven British firms (not explosives manufacturers) who kindly supplied information as to their processes for nitric acid manufacture—

4 use the Valentiner—with S-pipe modification.
4 „ S-pipe—silica ware or acid-resisting iron.
2 „ Waltham coil.
1 uses the Guttmann—with silica ware pipes.

Water Supply to Condensers.

Where water is required to drip over the condensing surface it may be supplied in perforated pipes, supported horizontally over the condensing system, as shown in Fig. 37, p. 67. In order to prevent blocking of the holes by sedimentation, it is advisable to have these on the top of the pipes rather than on the bottom. Iron pipes readily corrode and do not give good service. Aluminium pipes are found to answer very well.

Difficulty in ensuring a perfectly horizontal pipe often leads to unequal distribution of the water from the perforations, and a surer distributing system consists of a wood trough of triangular section, with serrations along the top edges. The overflow from such a trough gives a very satisfactory supply for condensing purposes.

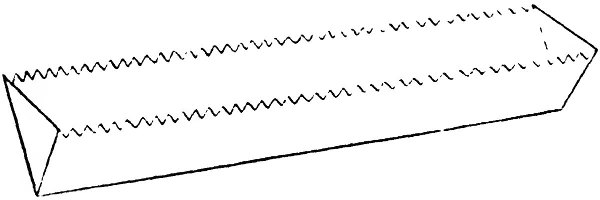

FIG. 51.—Water Distributer.

With the silica coil condenser it has been found that the provision of a fine spray of water from one or two centrally situated spray nozzles gives a more economical wetting than a drip distribution. Compared with the drip system, a water consumption saving of 50 per cent. resulted at H.M. Factory, Queen's Ferry, by the use of two sprays, one above and the other below, both spraying towards the centre of the coil. The types of spray used in sulphuric acid chambers or for the Gaillard concentration towers are quite suitable.

Fume Main.

Following the condenser proper, it is necessary to provide a pipe system to carry the uncondensed gases to a suitable absorption system, where the nitrous gases resulting from decomposition of HNO_3 can be oxidised and absorbed in water to give a solution of nitric acid. This pipe system is conveniently known as the fume main.

With an efficient condenser, the fume main is not called upon to undergo trying conditions of temperature change, and it may be constructed of good acid pottery ware. The ordinary spigot and socket pipes are used, joints being made as indicated on p. 78. Some nitric acid vapour gets over into this main and condensation takes place. This point should be borne in mind, and it is best to have the pipe line with a suitable slope so that the condensed acid can be drained away.

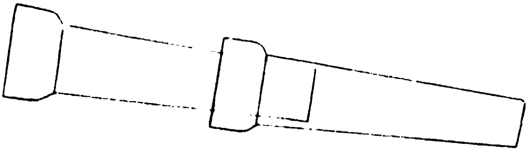

FIG. 52.—Tapered Spigot and Socket Pipes.

The fume main is best supported in two wood runners, with comfortable space between for remaking joints, patching pipes, etc.

At suitable intervals, water manometers should be inserted in holes in the fume main, being plugged in with asbestos cord and asbestos silicate cement.

Acid Mains.

The acid from the condensers is carried quite satisfactorily to the receiving vessels in acid pottery ware pipes, though both Narki ware and silica ware pipes are used with success for this purpose. It is as well to have a piece of glass pipe suitably placed in the acid main so that the rate of make of acid can always be seen. In all cases spigot and socket pipes are best, and the joints are made as indicated on p. 78. Special mention is made here of a tapered spigot and socket pipe, which has proved exceedingly valuable in carrying nitric acid. With this pipe the acid does not readily get at the jointing material, and joints have a long life. In a communication from H.M.

Factory, Greetland, Mr Ogg, the Acids Manager, writes of these pipes as a great success, and says: "The nitric acid mains at Greetland have stood a test of eighteen months' working without a single breakage, and most of the joints did not require repacking during the whole period."

It is very necessary in carrying nitric acid along jointed pipe lines to see that the line has plenty of fall, so that there is no tendency for acid to lodge. Unfortunately, designers and builders of plant often do not realise the nature of nitric acid, and are quite prepared to construct acid mains with a minimum fall. This point should be watched.

As there is always the possibility of burst joints or of broken pipes, it is a good plan to avoid woodwork in carrying acid mains, if possible. A light, acid-proof brick or tile support is suitable.

Questions such as whether to provide two independent acid mains with a suitable arrangement of taps for strong and weak acids; whether to equip each retort with its own receivers, or to provide common receivers; whether to cool the acid immediately after the condenser, or to convey the make of several condensers to a common cooler, etc., necessarily depend on particular requirements.

Cooling the Acid.—Cooling of the condensed acid is usually effected in lead, silica, or silicon-iron coils, or U-pipes. Lead can be used only for acids of over 88 per cent. HNO_3 content.

Acid Receivers.

Whatever their nature, nitric acid receivers should have fume-tight lids, their acid entry pipes should be securely luted and necessary openings for sampling or dipping purposes should be stoppered or provided with luted lids. Fumes from the receivers are conveniently carried by pottery pipes to the general fume absorption system. It is advisable to provide means for air or other agitation for sampling purposes.

It should always be considered bad practice to put nitric acid receivers in pits. Occasional trouble with leakage may be expected, and at such times pits are a great nuisance.

Pottery ware of a good acid-resisting type is the only really safe material in which to store nitric acid; but, because of its fragile nature and the difficulty of obtaining vessels of very large capacity, it is not by any means ideal. Pottery ware will store nitric acid of any strength, and is practically universally used for very weak acids.

Trouble of a greater or lesser degree is invariably experienced with the run-off pipes from earthenware receivers. Spigot type taps are usually led into corresponding socket holes near the bottoms of the tanks, and difficulty arises in making these taps leak-proof where inserted into the receiver. The usual method of insertion is to rely on a jointing of blue asbestos cord and soft putty with a facing of silicate cement, finally waterproofed with tar. Certainty cannot be ensured, but little difficulty is experienced if sufficient care, by one who understands the work, is given to the job.

To prevent destruction of platforms, supports, etc., it is advisable to provide a half-round tile drip drain where such outlet taps from earthenware receivers are situated. Such a drain can be connected by a suitable pipe line to a conveniently placed carboy or other collecting vessel.

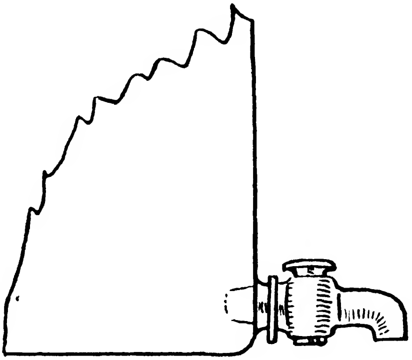

FIG. 53.—Spigot Tap in Earthenware Vessel.

Lead vessels may be used successfully for acids of 88 per cent. HNO_3 and over. Some corrosion occurs and lead nitrate is produced. This being insoluble in concentrated nitric acid, assists somewhat towards prevention of further corrosion. Lids of vessels do not get this protection, as the nitrate not being very coherent, readily scales off the metal and presents fresh surface for attack. Lead vessels should be built of stout sheet (20-lb. lead), and require to be very well stayed by lead-covered steel bands and railway metal girders.

Outlets from lead-receiving vessels are best controlled by earthenware cocks, a suitable type being the "block" variety, which is provided with a suitable iron frame for holding it in position and for holding down the plug.

Acid-resisting iron vessels are quite satisfactory for holding nitric acid, and where traces of iron in the acid are not detrimental, such vessels are successfully used.

Aluminium.—Seligman and Williams[1] show that cold nitric acid may be stored and transported in aluminium vessels. Dilute acid attacks the metal rather more than concentrated. Hot acids, on the other hand, must not be handled in aluminium vessels, as such acids of all strengths have considerable action on aluminium.

Iron and Steel.—Cast iron tanks are occasionally used to hold concentrated nitric acid, and where the nitric acid produced is required only for mixing with sulphuric acid, it is sometimes found convenient to run the acid into mild steel vessels containing sulphuric acid and provided with stirring gear. In this way an "approximate" mixed acid is obtained which can be adjusted as required (see Mixed Acids, Chapter V., p. 269).

Acid-proof Bricks.—Where the necessity has arisen for holding large stocks of weak nitric acid, built-up tanks of acid-proof bricks or tiles, and special cements (see p. 128) have been used with more or less success. Tongued and grooved tiles are useful in this connection. With suitable care such tanks may be made acid-proof, but if special attention is not given during the building by someone experienced in nitric acid work, there is great danger of the result being unsatisfactory and a continual source of worry. For all purposes where acid-resisting qualities are desirable, such bricks and tiles as "Nori" ware made by the Accrington Brick and Tile Company prove exceedingly satisfactory.

Materials of Construction.

1. **Pottery Ware.**—The earliest nitric acid condensers were made of pottery ware, but it was soon found to be deficient in the necessary qualities. It did not successfully withstand the temperature effects; it was inclined to be porous, and it was very lacking in the qualities of heat transference. As these defects were noted, improvements in the ware were effected to meet the requirements of the nitric acid process, and present-day pottery ware specially provided for nitric acid work is a much more reliable and satisfactory material.

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[1] *J. Soc. Chem. Ind.*, 1916, **35**, 665-672.

During the war a large quantity of inferior pottery ware was put to use in nitric acid work, but material supplied by long-established firms could generally be relied on to do what was expected of it. Doulton ware, for example, is a good acid-resisting pottery successfully used for nitric acid work. A comparatively recently introduced ware by Shanks is very close-textured and thin-walled, and has proved satisfactory in use.

Pottery ware may now claim to be acid-resistant and non-porous, but it often fails to withstand the necessary temperature changes during the condensation of hot nitric acid vapours. The rate of heat transference through pottery ware is not good, and in this sense it falls short of an ideal condensing medium. It is not sufficiently reliable in use, and condensing systems built of it are costly to maintain.

2. **Ceratherm.**—Ceratherm ware is claimed by the makers to be of porcelain quality as regards acid resistance, and to have a much higher thermal conductivity than pottery ware. It withstands violent changes of temperature without cracking. This ware, apart from a tendency to porosity, has, to the writer's knowledge, proved a satisfactory material for nitric acid condensation work.

3. **Glass.**—Glass is successfully used in the Hart condenser, and for sight-glass purposes in other condensing systems. A specially strong variety capable of withstanding sudden changes of temperature is necessary. With improvements in this type of glass, it could be used to a much greater extent in future condensing plant, thus enabling the process of condensation to be watched more closely.

4. **Silica Ware.**—The introduction of large scale plant of fused silica ware promised to prove of great value to nitric acid makers, because it was expected that the property of resistance to rapid changes of temperature would ensure reliability for condensing purposes. The expectations were very largely realised, and silica ware condensing apparatus was largely introduced in replacement of pottery ware. Silica coils proved particularly successful.

Silica ware is absolutely resistant to acid attack, quite non-porous, and is very successful in withstanding temperature changes. It has not a high thermal conductivity, however, and is sensitive to shock or strain, being very brittle. Its first cost is much higher than that of pottery.

With a suitable type of apparatus which lends itself to successful manufacture, fused silica ware is undoubtedly a very fine material for nitric acid condensation purposes.

5. **Acid-resisting Irons.**—The production of an acid-resisting iron may be considered a necessary step in the progress of evolution of acid works construction material. It is one example of man's adaptability to conditions with which he has to contend. Pioneers in this particular development of structural material had a difficult task, and the process of evolution has been comparatively slow. Nitric acid makers have cause to be deeply indebted to those who have produced such an eminently useful material as an iron which will successfully withstand the corrosive action of nitric acid.

Specially named iron alloys containing a high percentage of silicon are now available for nitric acid condensing purposes, *e.g.*, Ironac, Tantiron, Elianite, Duriron, and Narki. These alloys are highly acid-resistant, non-porous, and successfully withstand the changes of temperature to which nitric acid condensing plant is subjected. They are very brittle and have to be handled almost as carefully as pottery ware. Their thermal conductivity is much higher than that of pottery or silica ware, and this is of great advantage for condensation purposes. Their density is very high compared with pottery ware, and necessitates very substantial structures to carry the condensing units.

As an indication of the value of Narki ware for intensive nitric acid retort work, the following comparison of costs is interesting. At H.M. Factory, Gretna, the total cost for material and maintenance of twenty-four retorts for one year, vertical uptake only, in pottery ware was at the rate of £1207 per annum, of which £530 represents labour. The cost of material and labour in replacing this pottery ware by Narki metal amounted to £352. Subsequent maintenance charges on the Narki plant were practically nil over a period of two years. In addition to actual cost figures, the advantage of continuity of output with Narki ware was of great value at a time when enormous demands for nitric acid had to be met.

Selection of Materials.—In regard to selection of materials of construction, no hard and fast rules can be laid down. It must be generally accepted that with suitably built apparatus, acid-resisting irons are most satisfactory in use. With reasonable care in handling, and with careful attention to assembling so that the material is not subjected to irregular strain, there need be no fear of breakage from one year end to another. The suitability of the particular apparatus supplied is by now fairly well assured as a result of close study on the part of those who have used, and those who have made, such acid-resisting ware. Care in assemblage of the parts is vital, and lack of attention here should not lead to complaints against material. If one will handle the metal as if it were glass, good results will follow. Such irons are very costly and very heavy, and therefore their use is not usually extended beyond what is necessary to ensure security against breakage of material. Where temperature variations are small, acid pottery ware may be used with advantage. Notwithstanding their very high degree of acid resistance, high silicon irons do dissolve to a slight extent in nitric acid, and where it is essential to produce an acid free from iron it is not advisable to use them for condensing purposes. The traces of iron actually dissolved are so small, however, that acid condensed in acid-resisting iron ware will pass most specifications.

Fused silica ware is exceedingly valuable for nitric acid condensation purposes. It is not quite as immune to breakage during plant working as acid-resisting iron, but if it is carefully assembled and not subjected to irregular strains, condensing sets of this ware will last for very long periods. Its heat conductivity is much less than that of iron ware, but it has the advantages of not giving any impurity to the acid and of not being so heavy as iron ware. Owing to high initial cost it is not desirable to extend the use of silica ware further than is necessary to ensure freedom from constant breakage. When the temperature variation is slight, it is again possible to use acid pottery ware.

Ceratherm ware has not been tried out to the extent of silica ware, and it remains to be seen whether the better heat-conductivity which is claimed for it will justify its extended use. It is not quite as fragile as silica ware, but it is usually more porous. Like silica ware it does not contaminate the acid.

Pottery ware will not withstand, with any degree of certainty, the trying conditions of rapid temperature changes which occur in nitric acid distillation. Although it is much cheaper to instal, the cost of maintenance and replacement, the waste of acid and fume and consequent destruction of plant and injury to the health of workers, more than outweigh the cost of a safer material. With slow working of the distillation process, the breakage bill with pottery ware might not prove excessive, but even this is uncertain. Good pottery ware specially made for nitric acid work is very satisfactory in use where rapid temperature changes are not met with. For example, after the first heat has been removed from the gases from the retort in iron, or silica ware, such pottery ware will stand well to condense moderately heated vapours and to convey the uncondensed gases away for absorption and to the exhaust chimney. Pottery ware also carries the condensed acid quite satisfactorily.

The glass tubes used in the Hart condenser give reasonable wear, but are always subject to breakage.

DELIVERY OF ACID FROM RECEIVERS.

Gravity Flow.

In a well-designed plant the receiving vessels are at such an elevation that the finished product can often be run by gravity to its immediate destination, whether it be some works process at an adjacent plant or to containers for despatch to distant parts of the factory, or to places away from the factory.

Such gravity flow is not always possible, and it is then necessary to move the acid by mechanical means. For this purpose pumps, acid elevators (either discontinuous or automatic), and air lifts are made use of.

Pumps.

High silicon iron centrifugal pumps for nitric acid work have proved very successful, and no one need be troubled in conveying nitric acid of any strength when such pumps are used with pipe lines of similar metal. Mr Ogg informs the author that one Ironac pump at Greetland pumped 3000 tons of 65 per cent. nitric acid, and was apparently as good as ever when the factory closed down.

The Ceratherm armoured centrifugal pump is said to be suitable for pumping nitric acid of all strengths.

Centrifugal pumps are now generally supplied with only one gland, and that on the suction side. This gland is subject to practically no acid leakage, and the old-time gland packing troubles are done away with.

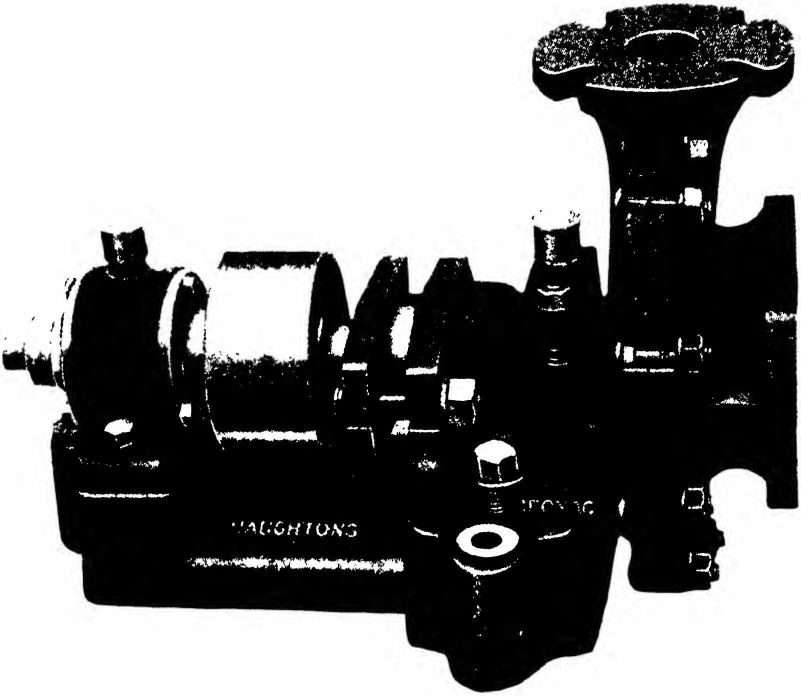

FIG. 54.—"Ironac" Centrifugal Pump.

Elevators.

Where elevators are used for conveyance of nitric acid they may be made of earthenware or acid-resisting iron. It is often more convenient to rely on automatic elevators than to be compelled to have a constant eye to the filling and discharging of the discontinuous type. Such automatic elevators can be obtained in stoneware and in silicon iron, and are claimed to be very satisfactory in use. Where they are well fitted, and when provided with a little patient attendance, they can be relied on to give good service.

Air Lifts.

The air lift is very commonly used in the circulation of nitric acid in connection with fume absorption (p. 101), but otherwise it finds little application.

Storing and Handling Nitric Acid in Carboys.

The carboy, of glass or earthenware, is a popular container for nitric acid. When properly packed with straw in a sound iron crate, it can be handled conveniently and with little danger of breakage. The earthenware variety is much less liable to breakage, but it possesses the disadvantages of non-transparency and extra weight.

When concentrated nitric acid comes in contact with straw there is great danger of fire, and as a safeguard the straw packing for carboys should be kept well wetted with water.

Carboys containing nitric acid should be provided with earthenware stoppers well luted in with moist clay, or luted with plaster of Paris and covered with moist clay, over which a cap of sacking should be secured (see p. 202). They should be stored independent of other materials on a floor where they can be drenched with water as required, and where protection from the sun is provided.

BUILDING TO HOUSE THE DISTILLATION PROCESS.

Foundation.

Retort settings with their retorts are heavy structures, and if trouble is to be avoided later ample foundations should be provided. If stability is not ensured from the beginning, trouble can be looked for in many directions when the plant is running. Levels will alter and it may be difficult to maintain the necessary slope on the pipe lines conveying acid. Pipe supports will sink and breakage will result from undue strains.

Enclosing Building.

Generally speaking, for comfort and security of working, the distillation plant, from the charging of the retorts to the receiving of the acid, should be properly housed.

Formerly, this question of housing was sadly neglected, and nitric acid plant was a hotchpotch in a roughly thrown together shed, with a maze of pipes situated in positions reached only by the performance of acrobatic feats on the part of the workers. In those days nitric acid production came to be looked upon with horror both by masters and men. There is no reason whatever why it should be looked upon otherwise than as a normal and reasonable works operation, and conditions should be such as to enable one to inspect every detail of the plant comfortably and without fear of one's life from gassing, acid splashing, or dangerous pitfalls. Such conditions do exist on well-arranged and properly conducted plants.

For these conditions, a good, roomy, well-ventilated building is essential. The skeleton structure may be of steel, but it should be as open as possible, and built with a minimum of members.

Materials.—During distillation a little nitric acid vapour invariably gets into the atmosphere, and this with the steam from the condensing sets produces weak nitric acid which readily attacks steel, entailing considerable trouble and expense in painting. Until non-rusting chromium steel is used for structural work, or until a true acid-resisting paint is produced, steel cannot be considered a satisfactory material to have in a nitric acid house. Provided due attention is paid to painting, however, the skeleton structure of steel may be relied upon to remain good for a longer period than is usually allotted for normal depreciation of acid plant buildings.

The roof should be fairly lofty, and well ventilated, and is preferably constructed of wood. Wood suitably coated withstands the action of nitric acid fumes as well as, if not better than, the best of any so-called acid roofing material available.

ROOFING MATERIALS.—As a result of testing fifty-one specimens of possible roofing materials for use on nitric acid plants, the author has come to the conclusion that wood suitably treated will give better service than any of the other materials tested.

The materials tested may be grouped into four broad classes, namely:—

1. Pliable roofing felts or fabrics impregnated with bituminous materials, or composed largely of bitumen.
2. Rigid roofing slabs, tiles, and slates consisting mainly of silicates (asbestos, cement, etc.).
3. Wood, treated and untreated.
4. Corrugated iron, treated.

These materials were suspended by asbestos cord from glass rods in the same laboratory fume chamber, with restricted draught, where nitric acid vapours, nitric acid reduction products, and steam were produced for eight hours on successive days over a period of six weeks. The test was a very severe one.

Of those tried, the best preservatives for wood proved to be :—

(*a*) "Solignum"—three coats applied with brush.

(*b*) "Solignum"—applied by soaking in a hot solution under reduced pressure.

(*c*) "Duroprene"—two, three, and four coats applied by brush.

(*d*) "Solignum"—one coat. "Duroprene"—two coats.

"Solignum" is a creosote oil preparation.

"Duroprene" is a rubber-like varnish manufactured by the United Alkali Company, and sold by A. H. Davis, Limited, Maguire Street Paint Mills, Liverpool.

To rainproof the roof a coating of an asphaltic material of the ruberoid type is very satisfactory, as it turns water and stands up well to acid atmospheric conditions.

Ventilation.—The sides of the building are best boarded, and ample provision for free passage of air should be made by having large permanent openings, except on the side receiving the full force of the prevailing wind where simple sliding doors might be used.

It is essential that there should be free movement of air through the building to assist condensation, but it is disastrous for pottery ware under working conditions to be subjected to cold blasts of air.

GENERAL PLANT LAY-OUT.

The simple diagrammatic representation of a nitric acid plant in Fig. 57 serves to indicate the general lie of respective

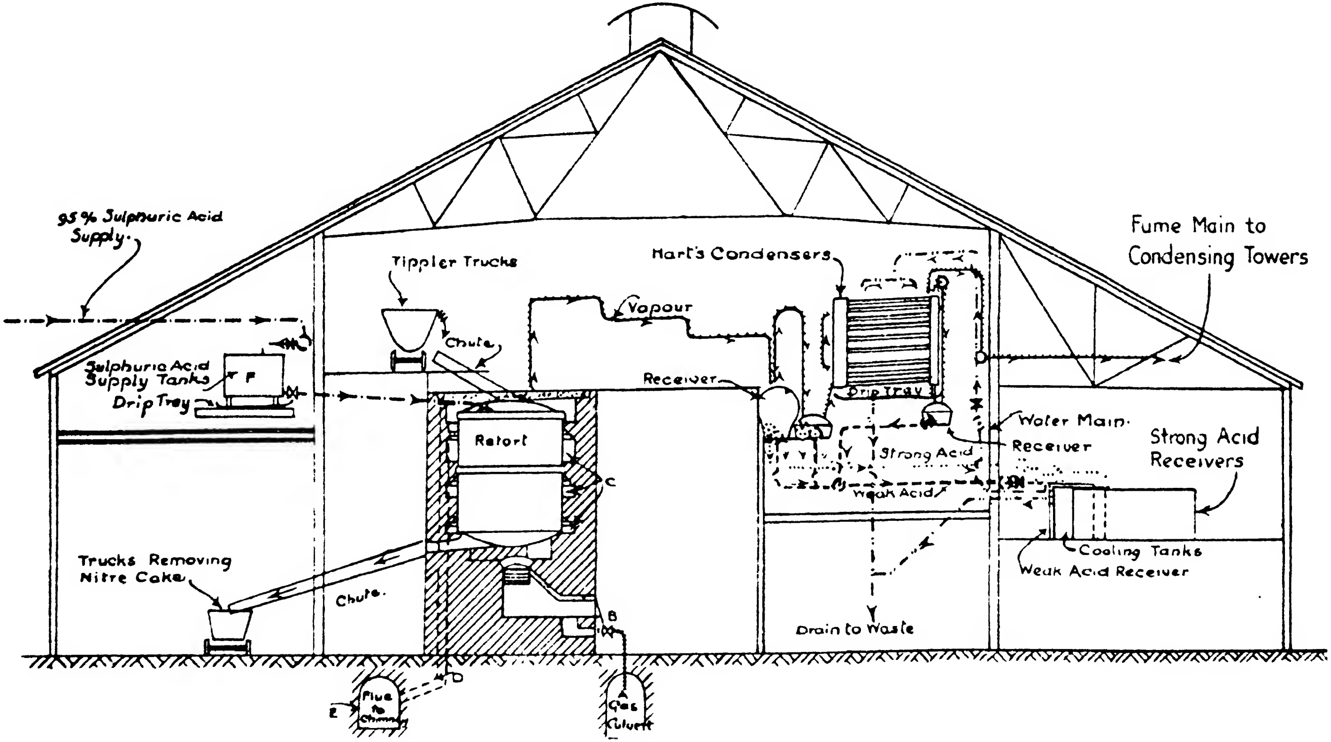

FIG. 55.—General Lay-out at H.M. Factory, Gretna (Early type).

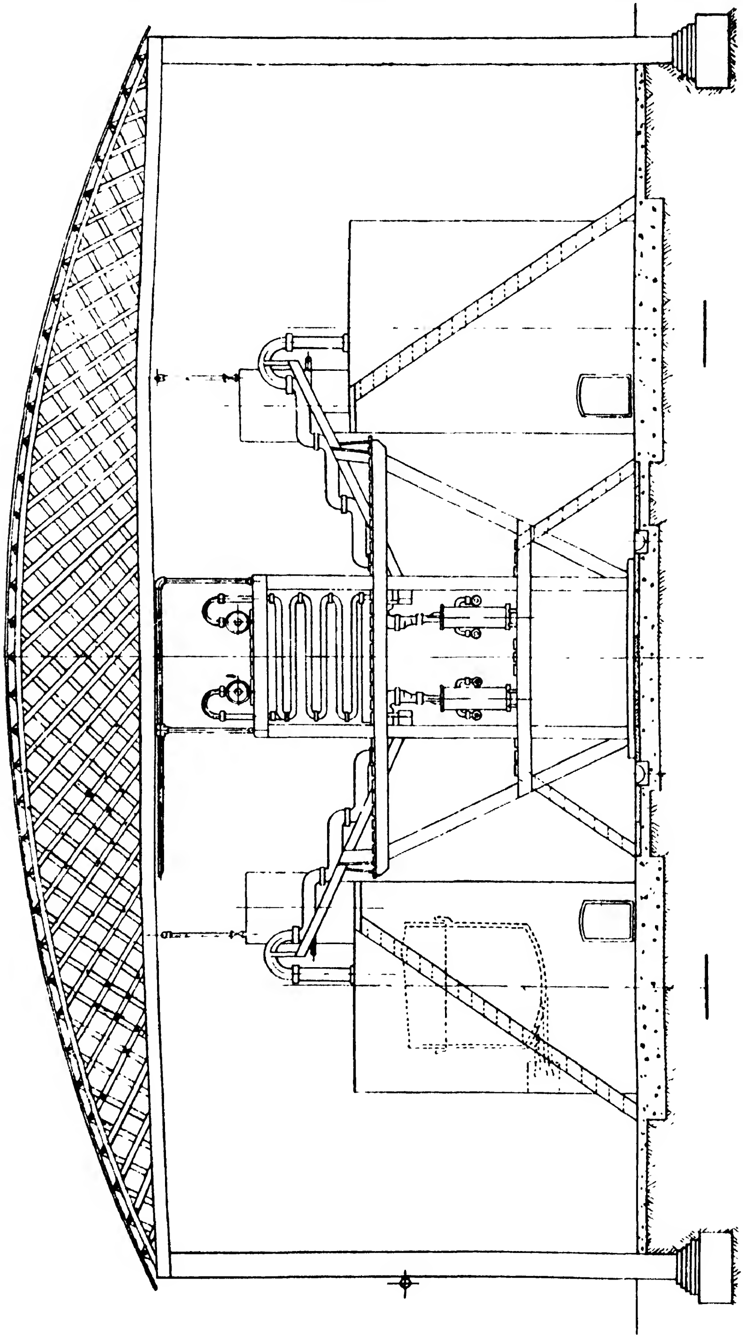

FIG. 56.—General Lay-out at H.M. Factory, Greetland.

parts, and shows where platforms are required. Platform A has to serve for the support of a container for the charge of sulphuric acid and to be the main promenade platform for general superintendence of the plant. Along the same platform is brought the charge of nitrate of soda for the retort. It is well to provide a hard-wearing material for this platform, such as steel chequer plate or hard surface bricks. It is best to have the platform clear of all encumbrances.

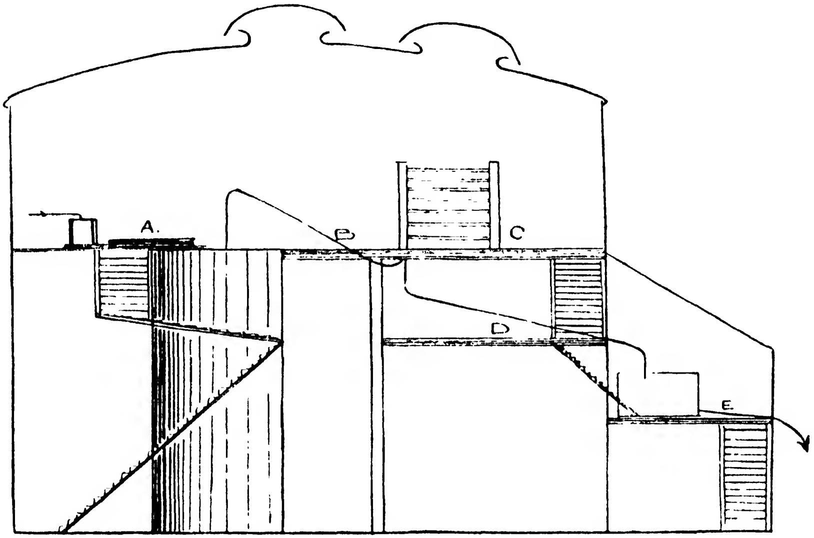

FIG. 57.—Diagrammatic Lay-out.

Platform B may be a light wooden gangway as it is only for the purpose of getting from A to C.

Platform C has to carry the condenser and the fume main, and must be proportioned according to the weight it has to bear. It should provide reasonable accommodation for free access to all parts of the condenser. It may be of wood or of reinforced concrete with acid-proof brick surface.

Platform D serves to carry the acid delivery main and cooler. It is necessary to use this platform for inspection of the bottom part of the condenser, and for the purpose of sampling the acid and taking specific gravities. Wood or reinforced concrete with acid-proof brick surface may be used for this platform.

The floor of the whole building should be of acid-proof brick or acid-proof tile slabs laid on concrete, and should have good slopes to drains.

Water Service.

Convenient water service should be provided at many suitable points through the building, and tubs containing water should be available for use in cases of acid burns.

DRAINS.

The drains should be open half-pipe or acid-proof brick or tile channels, and where necessary should be covered with wood battens. To have open drains is advantageous, as they are then always easy of access and the effluent is readily inspected. Systematic tests for acidity serve to check loss of acid.

ABSORPTION SYSTEM.

The Gases.

The fume passing forward from the nitric acid condenser consists chiefly of nitric acid vapour, water vapour, nitric oxide, nitrogen peroxide, nitrosyl chloride, and chlorine, the latter two being present mainly during the first working of the charge and being due to the presence of chloride in the nitre. Most of the nitric acid vapour condenses in the fume main, but no degree of condensation will produce nitric acid from the remaining nitrogen containing gases. Alternate oxidation and water absorption are necessary for the conversion of these gases into nitric acid.

Reactions involved in Absorption.

Different views are held as to the reactions which take place in the conversion of nitrogen peroxide by water and oxygen of the air into nitric acid.[1]

According to Burdick and Freed,[2] the process consists of

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[1] E. K. Rideal, *J. Ind. Eng. Chem.*, 1920, **12**, 531-8.

[2] C. L. Burdick and E. S. Freed, *J. Amer. Chem. Soc.*, 1921, **43**, 518.

two important reactions. In the first place nitrogen peroxide reacts readily with water to give nitric acid and nitric oxide.

$$(1)\ 3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO.$$

The proportion of NO_2 converted is promoted by increase in concentration of the NO_2 but hindered by increase in concentration of NO, increase in concentration of HNO_3, and rise in temperature.

In the second place nitric oxide is oxidised, by the oxygen of air supplied, to nitrogen peroxide which then undergoes a similar cycle of reactions.

$$(2)\ 2NO + O_2 = 2NO_2.$$

It is seen that the two molecules of NO_2 produced in reaction (2) result from the introduction originally of six molecules of NO_2 to the cycle, and in each successive cycle one-third of the original NO_2 becomes reconverted through NO into NO_2 again.

Absorption Towers.

The absorption process is conveniently carried out in earthenware pipe towers packed with distributing material such as quartz or special acid-resisting tile ware packings, and down which is circulated a supply of water which becomes converted into nitric acid. The liquid is conveniently circulated by means of an air lift which also serves to introduce the necessary air for oxidation purposes. The gases from the nitric acid condenser are passed through the absorption tower from bottom to top, and so to the stack provided for exhaustion to atmosphere. Occasionally such towers are made of acid-resisting irons. As in the reactions involved in the absorption process considerable heat is developed, and as absorption of NO_2 is effected more readily in the cold, it is desirable to keep the apparatus cool. Acid-resisting iron towers should be more lasting and more efficient than the stoneware ones, which, though very serviceable, are liable to crack. The great weight of iron towers is disadvantageous.

For cooling purposes it is advisable to have the absorption system open to the air.

The typical absorption tower consists of a saucer in which rests the first section of the tower, having a junction piece available for connection to the fume main and an opening to serve for a liquid run-off tap. This bottom section is left empty. As each successive section of the tower is built up, an

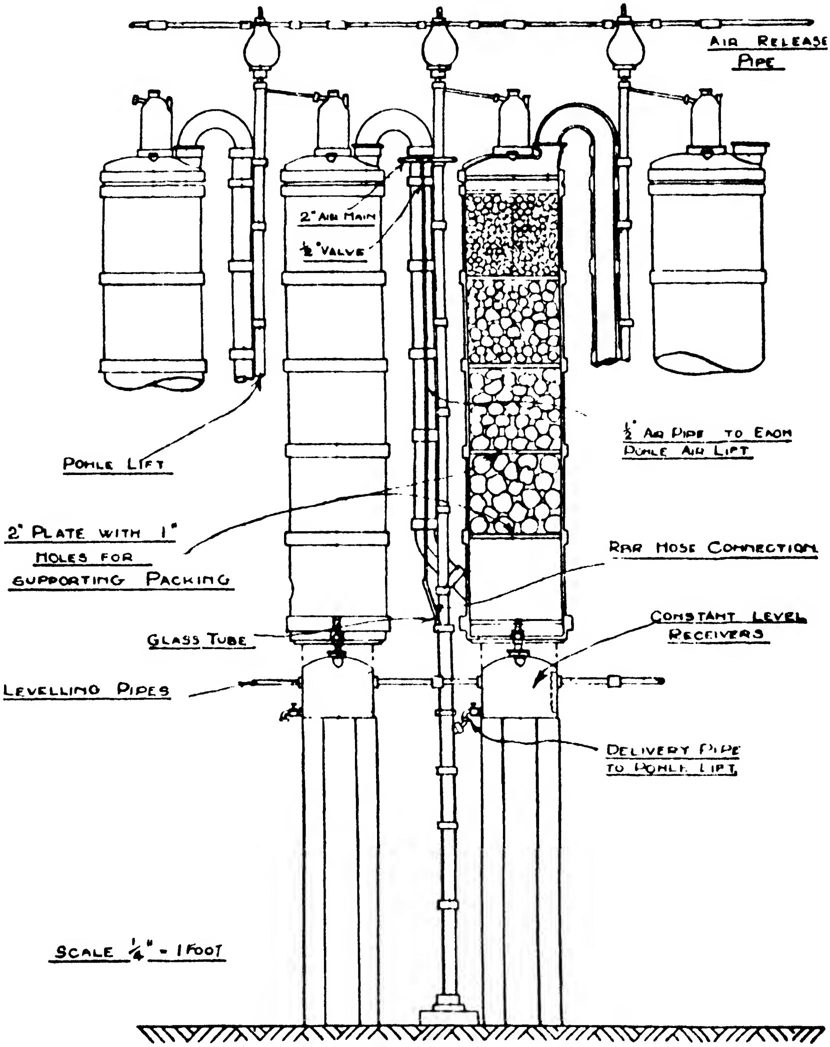

FIG. 58.—Absorption Tower System.

earthenware plate, perforated with a large number of 1-in. holes, is placed across the tower on a projection provided, to serve as support for the packing in the next higher section. The top plate may be a special liquid distributing plate. Above the lid a suitable distributing vessel (the "beehive") provided with bib cocks, serves to receive the circulating liquid and to pass it again to the tower, to a preceding or following one in a series, or to some other place as required. The sections of the tower are jointed with asbestos rope and soft putty, with a facing of Portland cement painted with tar.

The run-off tap from the saucer supplies an earthenware receiver, which is provided to ensure a constant supply of absorbing liquid to the circulating air lift.

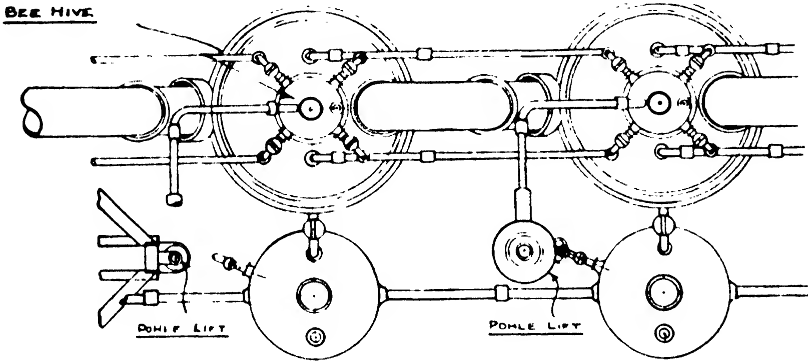

Fig. 59.—Plan of Absorption Tower System. To show possibility for distribution of the dilute nitric acid elevated by the Pohle lifts to the beehive distributing bottles.

The Air Lift.

The principle of the air lift is the balancing of a column of an air-liquid mixture against a smaller column of liquid, with the result that successive plugs of liquid are raised in a pipe by the admission of a supply of air in the form of bubbles at the base.

One type of air lift is shown in Fig. 60. The absorbing liquid from the receiver at the foot of the absorption tower is supplied into a junction piece of a 4-in. pottery ware pipe column which forms the well. Passing centrally down the well is a 1½-in. pottery ware pipe column ending at the bottom of the well in a fluted pipe. This 1½-in. column extends upwards out of the well to some distance above the lid of the absorption tower and finishes in an earthenware receiving-pot which serves as an air release trap. Passing into the well at the top, and running downwards alongside the 1½-in. column, is a ⅝-in. glass tube turned up about 3 in. at the bottom of the well under the fluted base pipe of the 1½-in. column. This glass tube is connected at the top to a supply of compressed air at a pressure of 10 to 15 lb. per square inch.

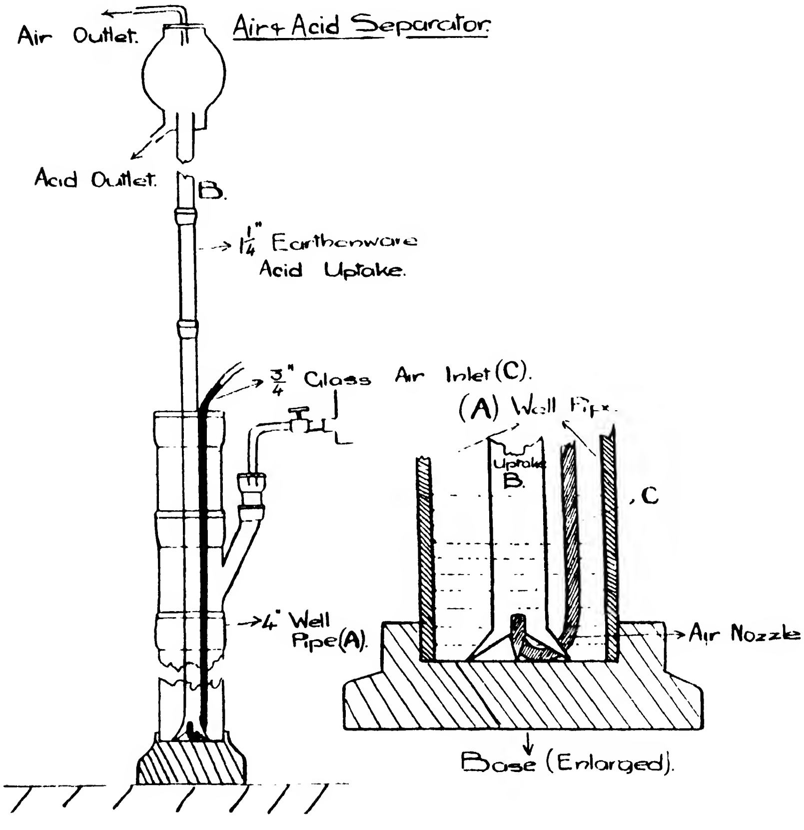

FIG. 60.—Diagrammatic Representation of Air Lift.

Fig. 61 illustrates a pottery Pohle lift well, moulded in one piece with air duct included. It was made for H.M. Factory, Bradley, by Messrs Kitson & Sons, Denby Dale, near Huddersfield, and proved very satisfactory.

With a supply of absorbing liquid in the well and admission of compressed air at the bottom, the liquid is lifted up the 1½-in. column, and delivered in successive jerky discharges into the air release bottle and thence back to the tower, or as required.

The "submergence" of the air lift, that is the ratio of the depth of the liquid in the well to the total lift desired, varies with a number of factors, but for lifts up to 100 ft. is usually about 60 per cent. Rather than have the wells of the air lifts in pits, it is advisable to build the absorption towers at a suitable elevation.

In working the absorption tower a sufficiency of water is admitted at the top, and this is circulated round the tower by the air lift. With uncondensed gases from the condenser system passing up through the tower, absorption, decomposition, and oxidation take place as previously indicated and the circulating liquid becomes dilute nitric acid. Effective absorption continues until acid of about 60 per cent. HNO_3 is obtained.

Acid of a much higher concentration cannot be obtained by this process, and at this stage the acid is run off to a suitable receiver and the absorption cycle is continued with fresh water. With a series of absorption towers at work, suitable adjustment of water-feed to the tower nearest the exit and of acid run-off from the tower first in the series allows a continuous stream of 60 per cent. nitric acid to flow from the absorption system to storage.

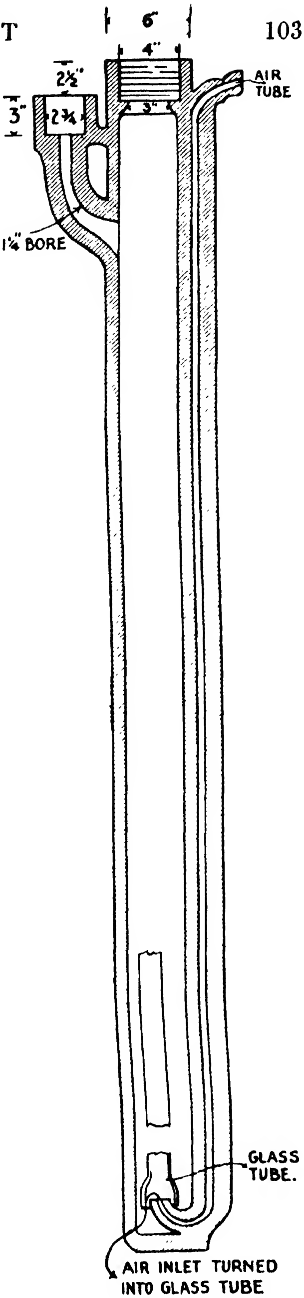

FIG. 61.—Pottery Well for Pohle Lift.

Tower Packing Materials.

The reactions carried on in the absorption tower are somewhat complicated, and it is very important to realise the necessity for time for these to take place. Where the reactions are in the liquid phase the time factor is a large one because of recirculation of the liquid. The chief gas reaction is $2NO + O_2 = 2NO_2$, and in preventing loss of absorbable nitrogen, facilities for this reaction must be provided. The time available for this oxidation is dependent chiefly on the velocity of the gases through the tower. If the tower, therefore, is closely packed, a good scrubbing surface which facilitates absorption of NO_2 is provided, but the reaction time for oxidation of NO_2 is diminished as the gases have to travel more quickly. The absorption of NO_2 is practically immediate, whereas the oxidation of NO is relatively much slower. It is necessary, therefore, that the packing of the tower shall be so adjusted that the best results are obtainable. From what has been said above, the tendency will be to provide the maximum free space consistent with adequate wetting surface.

In addition to the points already noted there is the question of resistance to gas flow to be considered. This resistance increases rapidly with decrease in size of material, and the provision of adequate wetted surface might result in destruction of proper conditions of draught.

In nitric acid work, coke packed towers are inadmissible owing to the reducing action of coke on the acid and consequent loss of nitrogen.

Quartz is unacted upon by nitric acid, and is largely used as a tower packing. It is often used in a number of graded sizes from 6-in. material at the bottom to 1 in. or less at the top. The quartz used for nitric acid absorption towers should be hand picked and as free as possible from non-siliceous matter, as disintegration of foreign materials during working may seriously impair the efficiency of the tower, and lead eventually to serious choking. By the use of quartz a high percentage of free surface may be presented to the gases by using small material, but resistance to gas flow is then serious and the percentage of free space is relatively small. Zeisberg[1] shows

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[1] *Chem. and Met. Eng.*, 1919, **21**, 765.

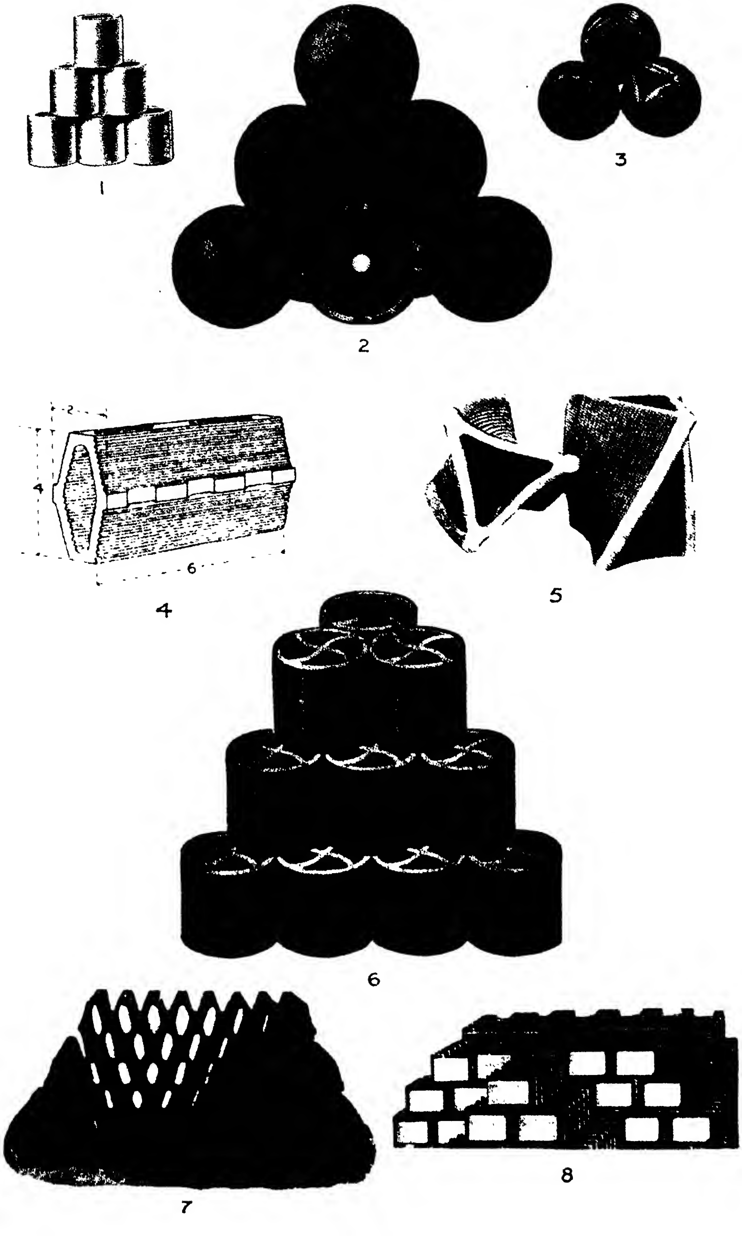

FIG. 62.—Types of Packing Materials.

[*Face page* 104.

that for a given size of packing quartz is not as good a tower packing as specially prepared regular packings.

Special tower packings made of acid-resisting brick and tile ware are made in a large variety of shapes, for which the makers claim certain advantages. A few types of packing materials are shown in Fig. 62. The author has found the partition ring packing of the Accrington Tile and Brick Company very satisfactory.

Tower Capacity.

As some indication of the necessary tower capacities for efficient absorption the following figures, which have come within the author's experience, are quoted :—

	A.	B.
Composition of inlet gases .	NO_2 = 33·0 per cent.; O_2 (necessary oxygen supplied by air of Pohle lifts) = nil.	NO_2 = 15·0 per cent.; O_2 = 8·0 per cent.
Temperature of inlet gases .	35° to 45° C.	45° C.
Reaction time	260 seconds	120 to 140 seconds
Tower free space . . .	1 lb. NO_2 per minute per 100 cubic feet free space	1 lb. NO_2 per minute per 120 cubic feet free space
Area of wetted surface . .	1 lb. NO_2 per minute per 6000 square feet of wetted surface	1 lb. NO_2 per minute per 5000 square feet of wetted surface
Efficiency of absorption . .	97 per cent.	91 per cent.

The question of tower capacity is carefully considered by J. A. Hall, A. Jaques, and M. S. Leslie[1] in a recent paper on Nitric Acid Absorption Towers.

Concentration of Acid Produced.

It is desirable to produce as concentrated a nitric acid as possible, but the concentration is limited in normal practice to about 60 per cent. HNO_3, owing to the retarding effect of NO on the reaction of absorption.

$$3\,NO_2 + H_2O \rightleftharpoons 2\,HNO_3 + NO.$$

According to Burdick and Freed (*loc. cit.*), with dilute nitric

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1922, **41**, 285-293.

acid absorption of NO_2 progresses substantially to completion, whereas with concentrated acid the presence of even a small proportion of NO completely inhibits the progress of the reaction. In this case, absorption can only proceed as the NO is oxidised by excess of oxygen present in the gases.

Effect of Chlorine on Absorption.

In an interesting report on "The Effect of Chlorine on Absorption by Water of Nitrous Gases diluted with Air" (Technical and Research Report II., H.M. Factory, Oldbury, Site A, dated 30th October 1916),[1] H. W. Webb gives evidence of a much more marked increase of HNO_3 content in one tower of a series in an absorption system than in the other towers of the same series. In investigating this matter he found that the acid solution obtained in the same tower showed a correspondingly marked decrease in HCl content. The results of one set of observations are shown graphically in Fig. 63, where it is seen that increases in HNO_3 content correspond closely with decreases in HCl content.

On the basis of his experimental investigation of the conditions in an absorption system for gases leaving the condensing system of a house of nitric acid retorts, Webb puts forward a theory of oxidation of nitrous gases through the intermediary of hypochlorous acid resulting from solution of chlorine in water. J. A. Hall, A. Jaques, and M. S. Leslie[2] consider that chlorine may both help and hinder the absorption of NO_2 under different conditions of acid and gas concentrations.

For further particulars in the study of absorption of oxides of nitrogen in water, the reader is referred to pp. 256, 264, and to Vol. VII. of this work, *The Fixation of Atmospheric Nitrogen.*

FUME EXHAUSTING SYSTEM.

In order to handle the uncondensed fumes from the nitric acid condenser satisfactorily, it is necessary to provide some means of exhausting them through the absorption system.

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 162-164.

[2] *J. Soc. Chem. Ind.* (*Trans.*), 1922, **41**, 285-293.

Vacuum Pump.

In the Valentiner process of manufacture the vacuum pump serves to do this (see p. 137), and owing to the necessity of keeping acid fumes from the pump, complete absorption must be effected before the gases reach it.

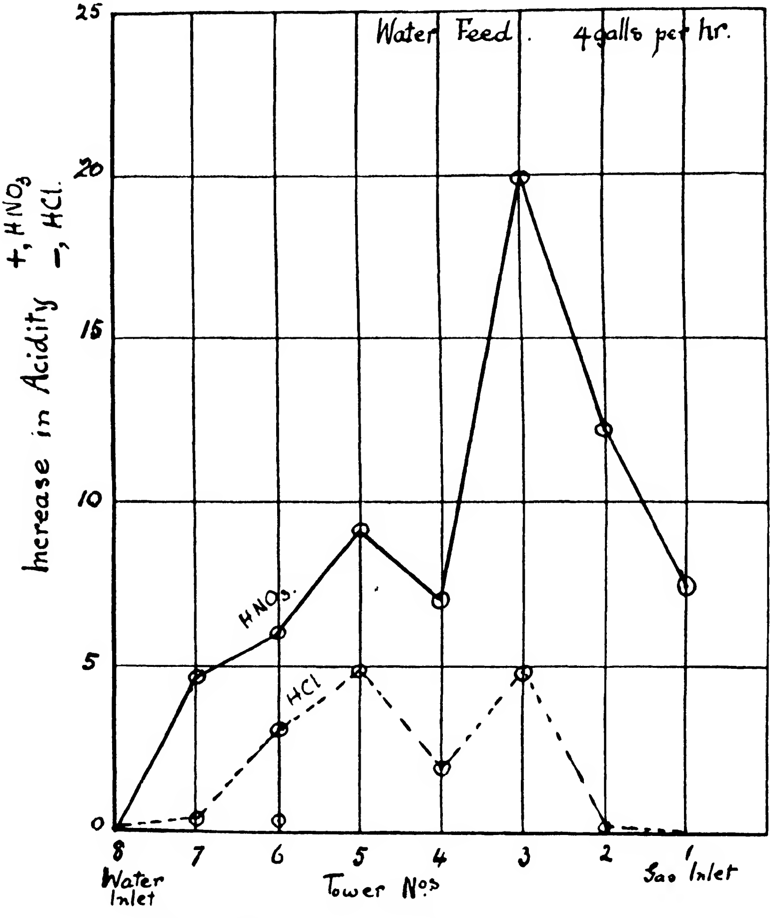

FIG. 63.—Effect of Chlorine on Nitric Acid Absorption.

Fans.

In processes other than the Valentiner, exhaustion of uncondensed fume is effected by a variety of methods. Direct exhaustion through an earthenware fan either before or after the absorption system proved satisfactory so long as the fan remained good. Owing to the uncertainty of such fans they are now little used. Similar fans of acid-resisting irons are now available and prove quite satisfactory in use.

Ejectors.

Much use has been made of the ejector principle in exhausting nitric acid fumes, and with complete success. Three methods are in use: (1) Ejection by compressed air, (2) by steam, and (3) by air at high velocity delivered from a fan. Using the ejector principle a much better result is obtained by having a well-designed ejector rather than a simple jet in a parallel fume pipe. Such ejectors can now be obtained either in chemical pottery ware or in acid-resisting irons. Fig. 64 illustrates a Narki ejector for use with steam or compressed air, while Fig. 65 illustrates the Campbell pottery ware ejector, as introduced by J. Campbell at Gretna for use with a blower fan. The Campbell ejector, which is very successful, is supplied by the Davidson Engineering Company, Belfast. Compared with fans, all ejectors are wasteful of power.

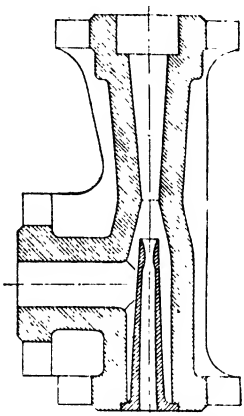

FIG. 64.—"Narki" Metal Ejector.

In working a charge of nitrate of soda, it is convenient to have a slight suction through the fume main to the retort, and to achieve this, attention is well directed to the means provided for fume exhaustion.

CONVEYANCE OF NITRE TO THE RETORT.

Some mechanical contrivance is advisable to assist in transference of nitrate of soda from the store to the retort.

Ideally the nitre store would be on the same level as the charging platform of the retort, but this is only rarely met with. In such a case the conveyance from store to retort is easily accomplished. If the nitre has to be conveyed and elevated it is often carried in the bags in which it was shipped,

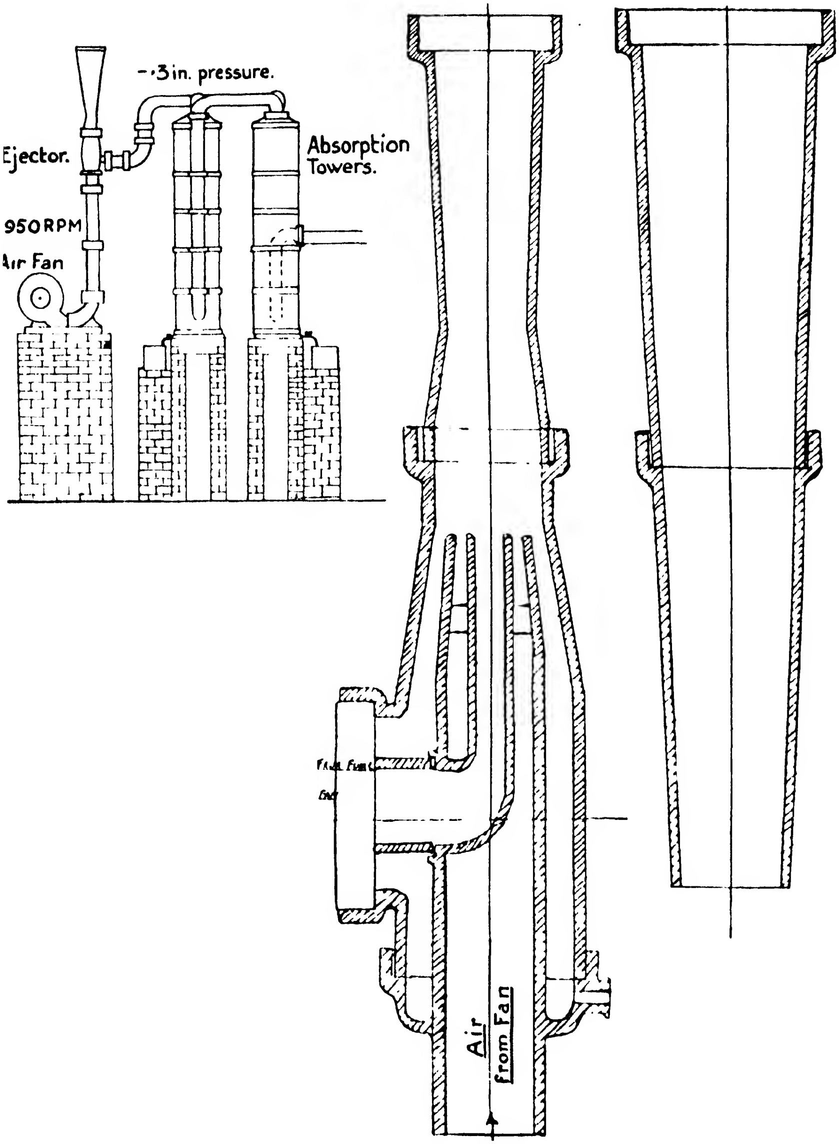

FIG. 65.—Campbell Ejector.

first being wheeled on hand trucks and then lifted by an arrangement of pulleys. If, however, it has been stored in bulk, it can be carried in sheet iron tubs or trolleys and lifted as before.

Where the nitre is dried, suitable arrangements for conveyance to and from the drier have to be made.

The problem of conveyance for large installations is relatively simpler, as it then pays to have bogies on rails or elevated runways in conjunction with hoists or some form of purely mechanical conveyer. In an article on Large-Scale Sulphuric Acid Manufacture,[1] the following description is given of a feeding system for nitric acid retorts: "Each retort is supplied with nitre by an automatic feed device motor driven, and geared to a lead wheel provided with lead cups burned to its circumference, revolving in a small tank of acid in unison with the revolutions of the worm which feeds the nitre, so that automatically, as the nitre is fed, the correct proportion of sulphuric acid is poured into the pot."

Weighing.

In any case it is necessary to supply the nitre to the retorts in weighed or measured lots as desired for the charge. Keeping in mind the fact that nitre bags after shaking retain 1 to 2 lb. of nitrate, it is seen that by weighing in the bags an allowance for this is necessary in calculating the charge.

Charging.

A sheet iron funnel-shaped chute is useful in charging the retort with nitre.

DELIVERY OF SULPHURIC ACID.

Storage.

It is advisable to have an elevated storage tank outside the retorts building for holding sulphuric acid, so that it can be run by gravity to the retort.

Measuring.

For each retort a lead-lined wood, lead, or steel vessel should be provided at a slight elevation above the charging platform

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[1] *Chem. and Met. Eng.*, 1918, **19**, 405.

and of sufficient capacity to hold the acid for one charge. This vessel should be accurately calibrated, so that the acid content to a certain mark is known when the density of the acid is known. The dip may be observed by an internally fixed lead scale, a suspended pointer, an external gauge glass, or any other suitable device. If a gauge glass is used it should be of ample diameter to avoid choking, and the connecting elbow should be fitted with a full bore cock which can be closed in the event of the glass being broken. The question of measurement of the acid charge should be well and clearly worked out, so that the operatives may have no difficulty in providing the correct amount. A gravity supply to the sulphuric acid charge tank is thus to be preferred to either pump or egg delivery, as the control is so much easier.

Since too big charges of sulphuric acid result in unnecessary loss, and too little charges give thick nitre cakes which will not flow from the retorts, it is seen that careful attention is necessary to ensure the proper charge of acid being supplied. At some works each charge of sulphuric acid is weighed before delivery to the charging tank, and this is an eminently satisfactory method. In other cases special devices such as floats are provided within the charging tank, so that by simple adjustment of the height of the float by a suitable lever working over a graduated scale, excess of acid beyond that necessary for the correct charge is caused to overflow through a pipe to a suitable receiver.

Charging.

A pipe connection should lead from the bottom of the charge tank through a valve to the top of the retort, where it may be permanently connected through a luted pipe to the retort, or where a movable supply pipe can be provided to convey the acid through the lid of the retort when desired. The permanent connection is advisable, and in making it provision for cleaning should be allowed for by using some such arrangement as shown. This supply pipe is preferably led under the charging platform so as not to be in the way.

It is advisable to run in the acid charge as rapidly as possible because if at any time intensive working is in progress and a hot retort has to be charged, the addition of a dribble of sulphuric acid results in decomposition of the nitrate commencing during the addition, and difficulty, especially if the charging is not by a permanent connection, is experienced in completing the charge. The supply pipe should therefore be of ample diameter.

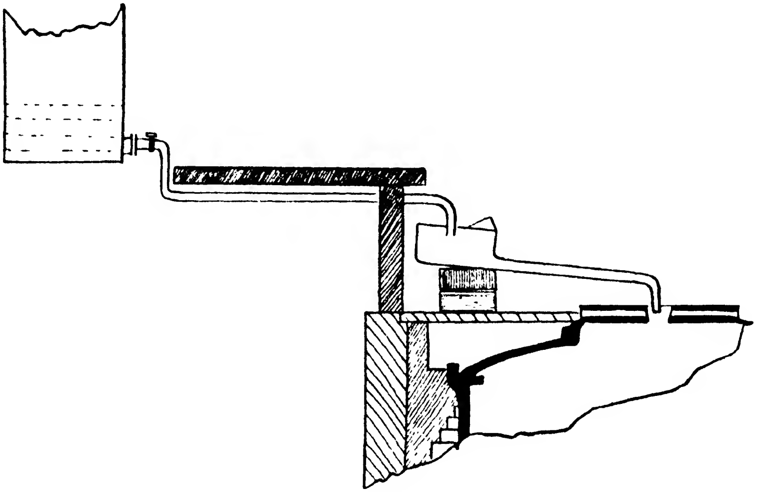


FIG. 66.—Supplying Sulphuric Acid to Retort (movable connection).

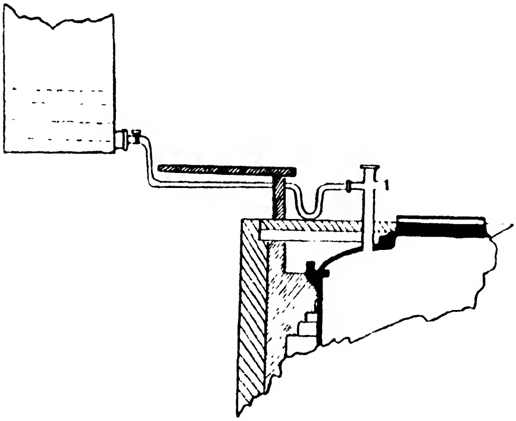


FIG. 67.—Supplying Sulphuric Acid to Retort (permanent connection).

METHODS OF FIRING RETORTS.

Naturally any source of heat which will bring about the required reaction between nitrate of soda and sulphuric acid, may be used for firing the retorts. Coal, coke, gas, and oil fires are commonly employed for the purpose. The distillation process requires very careful firing, and it is essential to have handy control of the fire. This is not a difficult matter whatever the fuel, but for simplicity and convenience, gas or oil may be considered superior to coal or coke.

With a coke fire a very evenly balanced heat supply may be given without any flame coming in contact with the bottom of the retort. The view is widely held that such heating conditions are ideal for nitric retort work, but as experience in gas heating is gained, it is seen that such a claim does not hold. Much has been said against the danger of gas flames impinging on the metal of the retort, and in many cases of gas firing special flame-breaking devices of chequered brickwork have been introduced into the combustion chamber. It remains to be investigated whether under parallel conditions of working one type of fuel or fire can be claimed certainly disadvantageous.

METHODS OF HANDLING NITRE CAKE.

Pans.

The nitre cake which is run molten from the retort at a temperature of approx. 200° C. is usually conveyed by suitably supported iron or steel pipes or troughs to shallow cast-iron pans elevated slightly from the floor, in order to allow air currents to pass underneath for cooling purposes. The pans have their sides sloping inwards, and dividing ribs across the bottom subdivide them into a number of compartments. The pan is designed to give solid nitre cake which will break up and leave the pan conveniently. A further assistance to removing the cake may be provided by having a stirrup-shaped piece of steel resting in each compartment of the pan. This gives an excellent grip

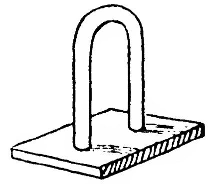


FIG. 68.

for crowbar work. When the nitre cake has solidified it may be broken up with sledge hammers and crowbars, and shovelled and handled out of the pans into barrows or trucks for disposal.

The disposal of nitre cake has always been a matter of concern. It may be dumped as waste material, utilised in some way on the works, or transported. The uses to which nitre cake may be put are considered in another place (p. 200).

The above outlined method for dealing with nitre cake is a heavy nasty job and requires much labour. Workers who handle the material should be well shod and clothed, and should have a liberal supply of pieces of sacking for use in handling.

The more conveniently arranged the provision for disposal is, the less will be the labour requirement and the more satisfactorily will the nitre cake be dealt with.

Danger.—Molten nitre cake is a very dangerous material, and workers should be specially warned of its character.

Trucks.

Sometimes it may be found convenient to collect the nitre cake in block form, and bogie trucks on rails may be made use of to receive it from the retorts. The truck should be cleaned before use and painted inside with a slurry of clay, or rubbed with grease or graphite in order that the block of nitre cake may be readily removed. Cooling in trucks is not nearly as rapid as in pans, and the blocks of nitre cake are not readily handled except by a crane. Before the nitre cake solidifies a hoop of iron is fixed in the molten mass to serve as a grip for removal of the cake when cold.

Powdering.

A very finely powdered nitre cake can be produced by stirring the molten cake mechanically all the time it is cooling in pans of the mortar mill type provided with rabbling arms instead of grinding rolls. Naturally this requires a lot of power, but the cooling period is much shortened. During the solidification there is considerable evolution of steam and acid vapours, and the fine flour-like powder produced gets widely distributed in the immediate neighbourhood. Special precautions are thus necessary to prevent undue destruction of plant and buildings by corrosion.

The product in this case is easily handled and transported.

Granulating.

A nice granular form of nitre cake is produced very simply by allowing the molten cake from the retort to flow from a chute in a thin stream, when, before reaching the floor, it is caught by a blast of compressed air from a horizontal slit in the supply pipe and blown into a shed provided for the purpose. The nitre cake is immediately solidified and falls to the floor of the shed in a fine sand-like powder. Solidified in this fashion the nitre cake is much less deliquescent than usual, and is comfortably handled without getting sticky. This method of granulation was introduced at H.M. Factory, Gretna, by R. P. Whitelaw.

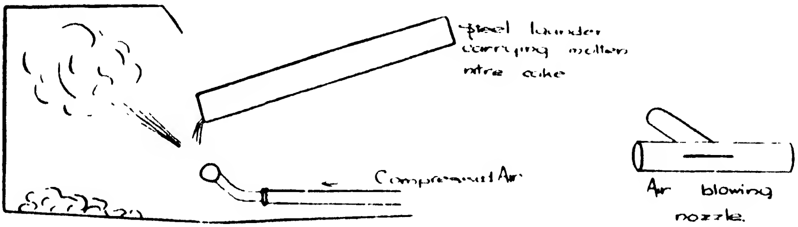


FIG. 69.—Granulating Nitre Cake by Air-blowing.

Dissolving.

Where deliberate waste of nitre cake is contemplated, and where conditions allow, the molten nitre cake may be run into a good stream of water and the solution run away to waste. This method is only possible in isolated instances where an outlet is available.

PLANT OPERATION.

In what has already been written the various parts of the plant and some details of operation have been considered. It is now intended to give a general outline of the actual process of manufacture of nitric acid, to be followed by descriptions of working conditions on various plants.

General Outline.

Before commencing the process of distillation it is essential to make a careful examination of the plant to see that all is in order. Nothing should be left to chance, since nitric acid and its decomposition products are nasty substances to handle, and it is as well to be assured that they shall remain within the particular pipes and tanks provided for them. Neglect of this examination may mean loss of material, destruction of plant and buildings, or even loss of life.

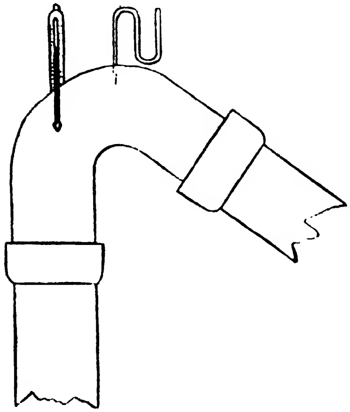


FIG. 70.—Thermometer and Manometer in Retort Uptake.

Guides to Control. — As guides to the control of the distillation, it is advisable to have a thermometer and a water manometer in the fume pipe leading from the retort. The manometer should be of reasonably large diameter glass tubing to avoid accidental plugging of the bore. These instruments are plugged into holes in the pipe by use of asbestos cord and asbestos silicate cement. They need careful attention to ensure non-leaking joints.

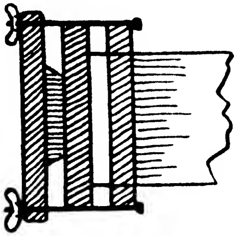


FIG. 71A.

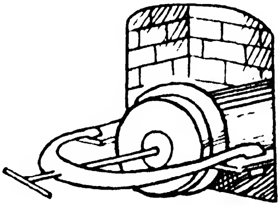


FIG. 71B.

Nitre Cake Outlet.—In commencing the distillation process one of the first points to attend to is the plugging of the nitre cake outlet of the retort. Assuming that the retort is empty, a ball of moist clay is inserted in the recessed end of the nitre cake outlet pipe and rammed in with a stick. An iron plug is then put in position and clamped against the outlet to prevent the clay from coming out.

Nitre.—The weighed charge of nitre is now introduced into the retort and then the man lid is put on, a thick slurry of clay being used to bed the lid, with a layer of Portland cement as a final luting.

Exhaust.—The exhaust system may now be started, and also the liquid circulation in the absorption system.

Sulphuric Acid.—If the retort is provided with a permanent connection for the sulphuric acid charge, the man lid may be solid. If not, a small central hole is conveniently provided for the admission of the movable pipe used for carrying the acid. This hole is plugged with a cast-iron plug luted in with clay and cement.

Before admitting acid to the retort a check is made of the quantity available in the charge tank, and then the required weight of acid is run into the retort and the valve controlling supply is closed.

An examination of the various manometers on the fume line will now indicate if all is in readiness for the distillation.

If so, a fire is lighted and well stoked until distillation begins. Water is now distributed over the condensers.

The Distillation.—As soon as the retort is warm, a few brown fumes appear in the condenser tubes, but distillation does not commence until the mass in the retort has reached a temperature of 100° to 110° C. The length of time for this stage to be reached varies with the temperature of the pot on charging and the intensity of firing. When distillation commences, the temperature in the uptake rises very rapidly to 90°-110° C., the change from warm to hot being easily detected by the hand.

The manometer also gives indication of distillation, the slight suction due to the exhaust system being converted into a pressure more or less pronounced.

The condensers show signs of steaming when distillation commences and condensed acid is soon observed.

The fire should be kept brisk in order to keep the distillation going, and the uptake temperature will rise steadily to 115°-125° C. When indications are given of a much more rapid evolution of vapours, after the distillation has progressed for about one and a half to two and a half hours (a time learned by experience), great care must be taken to reduce the fire and pay particular attention to the firing.

The temperature in the uptake may now be about 115° to 125° C., and a relatively quicker rise may be noted without increase of fire. The manometer gives signs of increased pressure. At the same time the atmosphere in the condenser system clears considerably, and very rapid condensation is effected.

THE "REACTION."—The distillation is said to be at the "Reaction" stage. Inattention to the firing in the initial stages of the "Reaction" leads to unsatisfactory results. If the signs of "Reaction" are imagined when not existent, and the fire is lowered too soon, the true "Reaction" is not properly developed and a long-drawn out distillation results. If, however, the true signs of "Reaction" are neglected and firing is continued, the evolution of vapours may become very violent, leading to boiling over of the contents of the pot, to uplifting of the lid, or to breakage in the condensing system. Such an uncontrollable "Reaction" is known as a "Blow." Violent distillations should certainly be avoided.

The "Reaction" period of the distillation is very important, and to have a good "Reaction" generally means a good distillation in all respects. The coal consumption will be low, the time of distillation short, and the proportion of strong acid to weak acid will be high.

Using the manometer largely as a guide, a steady, rapid evolution of vapours must be kept up—the fire being tended carefully to that end.

As the "Reaction" becomes less active, the uptake temperature gradually falls, the manometer pressure also falls, and the rate of distillation, as noted in a glass or transparent silica pipe leading from the condenser, falls off.

The fire must now be relighted or stoked up and an increased rate of distillation, though not so free as before, may be effected. The temperature in the uptake may now rise to about 140° C., and at this stage it will be found that the temperature will tend to fall even with a high fire. This indicates the completion of distillation.

The Condensed Acid.—A little dilute acid condenses in the initial stage of the distillation, but with the true distillation in progress the condensate soon increases in strength to the neighbourhood of 98 per cent. HNO_3, after which the strength only slowly decreases throughout the whole of the unforced distillation period. With the commencement of the increased firing period, the strength of the distillate decreases at a rather quicker rate, and during the last stages of the distillation the strength falls off rapidly. This is seen by reference to Fig. 72, which is taken from a report (undated) on "Experiments performed on the Gun Cotton Retorts" at H.M. Factory, Queen's Ferry, by N. V. S. Knibbs.

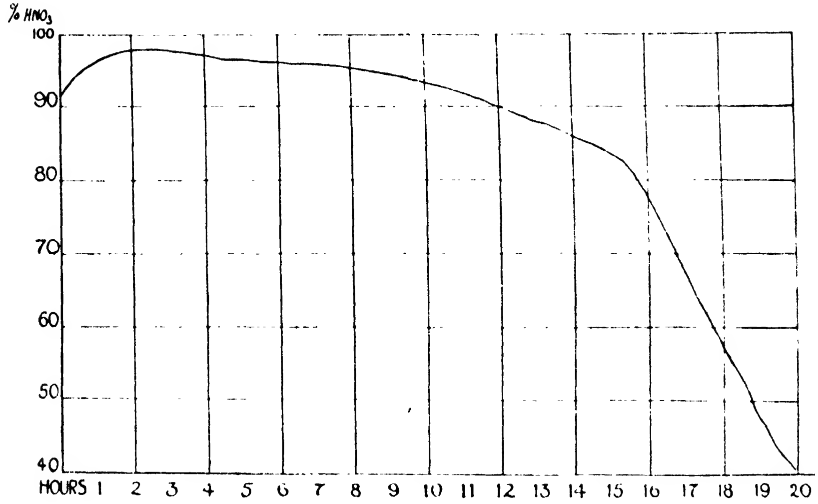


FIG. 72.—Strength of Acid Condensed.

Fig. 73, from the report on "Standardisation of Retorts, Silica Coils," by the same author, shows how the quantity of acid made varies during the progress of a distillation, being greatest at the "Blow" or "Reaction" period, after which it tails off gradually to the end of the distillation.

Where the condensed acid has to be collected in fractions, it is necessary to take samples of the condensate at intervals and determine its density, and from this gauge its approximate HNO_3 content. It is advisable to cool down the sample to 15° C. before taking its density, as the temperature correction

(0·0015 for every 1° C.) is not very reliable. When the acid is of the required density, suitable manipulation of run-off taps will serve to direct the flow of acid as desired.

Owing to the effect which the presence of dissolved nitrogen peroxide has on the density of nitric acid, it is not possible to determine the HNO_3 content by a density determination; but where conditions of practice are approximately the same, empirical rules may be developed and worked to for approximate purposes.

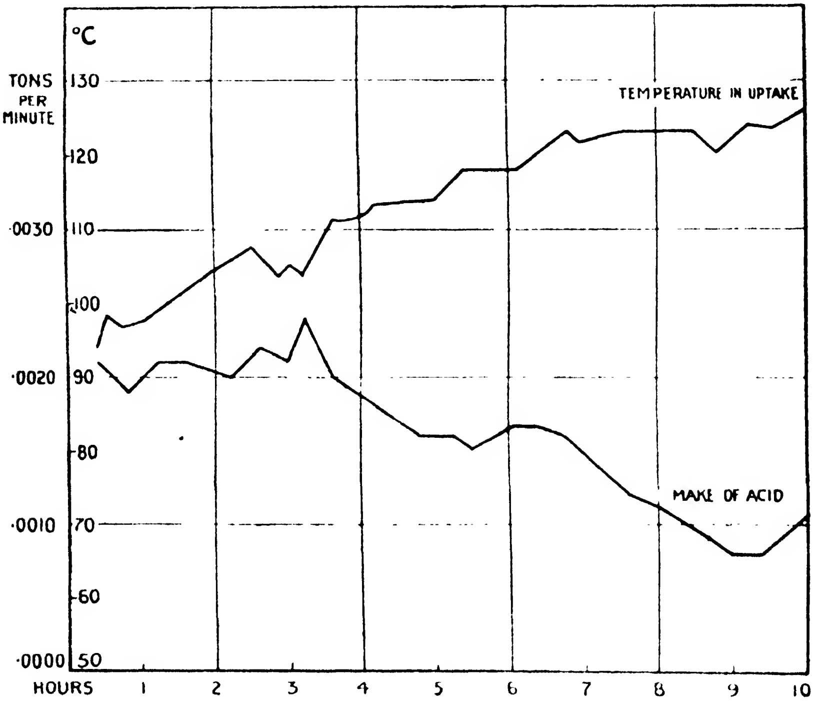


FIG. 73.—Temperature in Uptake and Make of Acid. Mean of Five Distillations.

For Specific Gravity Tables, see Chapter VI., pp. 325-328.

Absorbers.—During the progress of distillation, attention can be paid to the absorption system, where the circulating acid liquid can be tested for density and run off if necessary and fresh water supplied, or where increased rapidity of circulation may be applied to cope with rapid evolution of fume.

Tapping.—Completion of distillation may be assumed when the density of the condensate has fallen to about 1·340 at 15° C., when a pink coloration (due to iodine) is seen in the condensed acid, or when the uptake temperature cannot be maintained.

Note.—Crystals of iodine often collect in the condenser at the end of the reaction.

When the distillation is completed the nitre cake is run off. The discharge chute is first fixed in position. The iron plug is then removed from the outlet, and a worker, standing slightly at one side of the tapping hole, eases away most of the clay from the tapping hole with a steel bar. By pushing in a long steel rod from a distance the last of the clay is removed and the molten nitre cake flows out of the outlet.

Note.—Molten nitre cake is extremely dangerous, and workmen should be suitably cautioned as to the care necessary in dealing with it.

With the retort quite emptied and the run-off pipe clear of cake, the outlet can be replugged ready for the next charge.

Where more than one retort is working with a common fume main, it is necessary to damper off the fume main leading to any retort not distilling in order to keep the necessary suction in the remainder of the main.

The retort man lid may now be removed and cleaned ready for the introduction of a new charge.

Rate of Working.

For rapid working and to keep fuel consumption low, the retort may be recharged at once after ensuring that all is in order throughout the fume and acid systems. Normally such intensive working is not necessary, and taking everything into consideration it is not desirable. The addition of cold acid to a hot pot endangers its working life. Sufficient heat may be present to cause an immediate "Reaction," and this may result before the retort is securely closed.

Where batteries of retorts are worked practice varies as to whether all retorts are charged and distilled together, or whether each individual retort works its own cycle independent of the rest.

Progress of Distillation.

Fig. 74 shows three temperature records which serve to indicate the progress of a particular distillation. Platinum resistance pyrometers, connected to a thread recorder, were introduced (*a*) to the bottom of the retort and within the reacting mixture; (*b*) in the uptake pipe leading from the retort; and (*c*) in the top flue of the retort just where the waste gases were led away to the chimney.

It is seen that the temperature rise in the uptake at commencement of distillation is very marked. The effect of putting out the fire at 1.30 P.M.—at "Reaction" time—caused a temporary lowering of the temperature, which, however, soon rose again. After a steady temperature period following the "Reaction," the pot temperature rose steadily to the completion of the distillation. It is interesting to note that the pot temperature continued to rise after the fire was put out (*cf.* p. 166).

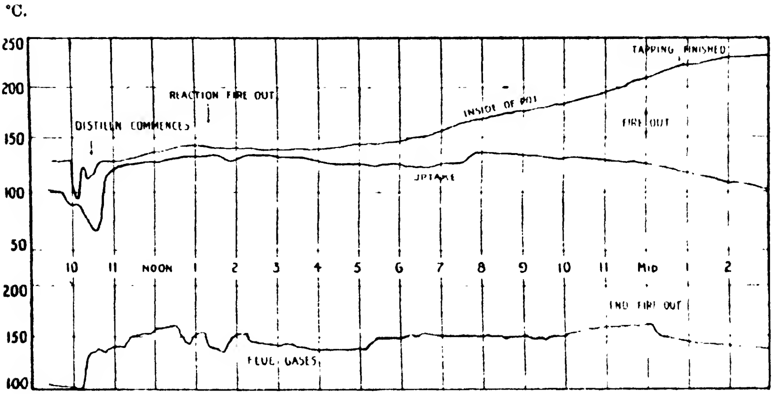


FIG. 74.—Temperature Records of Nitric Acid Distillation.

Use of Thermometer and Manometer.

In a report (undated) from H.M. Factory, Queen's Ferry, on "Standardisation of Retorts, Silica Coils," N. V. S. Knibbs gives a very clear account of the use of temperature and pressure indications in the uptake from a retort, and the following is quoted from his report.

The Temperature in the Uptake.—"The thermometer in the uptake gives us the first indication of when the retort begins to make. The temperature rises in a few minutes, probably 30° or 40° C. It will be seen by consulting graph No. 1 (Fig. 75) that distillation commences at various temperatures varying, in these experiments, from 82° to 105° C. But the temperature at which nitric acid distils must be nearly the same in all cases, so we are led to the conclusion that the temperature of the gases in the uptake is controlled very largely by the temperature of the upper parts of the retorts. Thus in distillation No. 1, although it had as good a fire under it as in Nos. 2 and 4, the curve of distillation is at a much lower temperature. This is no doubt due to the fact that the retort and brickwork were quite cold to begin with and the upper parts of the retort would take a long time to heat up.

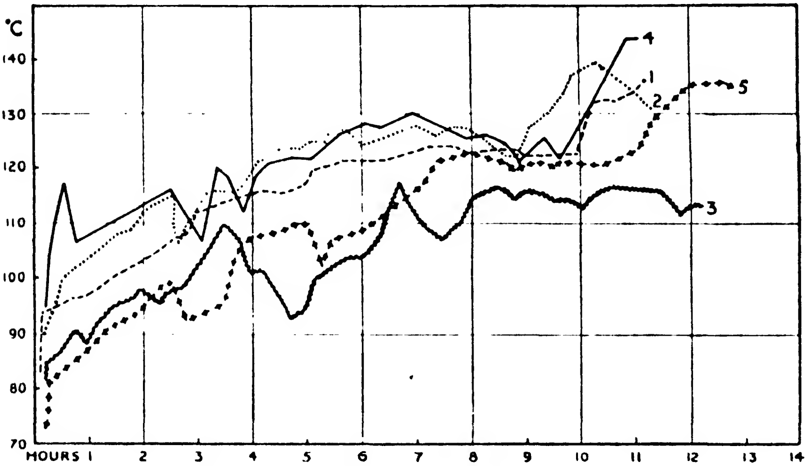


FIG. 75.—Temperature of Gases in Uptake.

"The contrast between distillations Nos. 2 and 4 and 3 and 5 is particularly strong. Nos. 2 and 4 were started with a good fire and here the nitric acid came over at a temperature well over 100° C., while in Nos. 3 and 5, after distillation had commenced, a small fire was used and nitric acid distilled over for two hours at under 100° C. It will be seen from the curves that the thermometer gives no indication of the proximity of a blow, though the temperature drops while the blow is in progress.

"The general tendency is for the temperature to rise fairly rapidly during the first two hours or more, then to drop suddenly during the blowing period, subsequently rising slowly and steadily for the next three hours before a gradual fall, until near the end of the distillation when it rises rapidly.

"The conclusion is that the thermometer in the uptake is of little use as an indication of the rate of distillation of the acid or as a warning of the proximity of a blow, and this is borne out by previous experience on the retorts. Its chief uses are to indicate the beginning of the distillation of the acid, and as a control on the temperature of the distilling gases, so that these do not reach too high a temperature. The aim should be to keep the temperature as low as is consistent with the proper rate of distillation, so that as little of the acid is decomposed by the hot sides and top of the retort as possible."

The Pressure in the Uptake.—"The pressure as indicated on the manometer was under ordinary conditions negative, that is, there was a suction in the uptake. This varied with the pull on the fume main which itself varied considerably, according to whether there were any retorts open at the lid. The result was that the manometer readings, when negative, had little significance except to indicate that the fan was operating properly, and that there was no blockage anywhere.

"When the retort begins to make rapidly, at the blowing period the pull on the manometer gets less and less until a positive pressure is registered. The manometer gives the first indication of the proximity of the blow, and it is here that its value lies. It also indicates clearly when the blow is over and it is safe to light the fire again, and this is of special value, as it is here that time is frequently lost.

"Without the manometer there is no guide to the violence of the blow, except the way in which the fume is blown out of the lid and other places, while with it we see at once the pressure developed and the necessary precautions can be taken without any unnecessary cooling of the retort by opening dampers, etc., a proceeding which is necessary only in the case of very severe blows, but which is frequently followed as a matter of safety in the absence of an indication of the probable violence of the blow."

Record of Retort Working.

A record of the working of a retort may be had by use of some such card as is here shown, which can be conveniently fixed near the top of the retort.

Retort Card.

Retort No.............................. Charge No.............................

Started charging....................... Date...

Finished charging...................... Ready to tap..............Date.......

Distillation commenced......... . ... Retort empty..........................

Charged by..................................... Total hours...........

Time.	Temp. of Retort.	S.G. of N.A.	Time.	Temp.	S.G.	Remarks.

The information on this card can then be posted to a sheet, such as is shown on next page, for permanent record of each particular distillation.

*Record of Retort No.*________________

Date when Charged.	Charge No.	Started Charging.	Times of Driving Retort.						Retort ready to be Re-charged.	Lost between Charges.	Remarks.
			Charging.	Heating to Distillation.	On Strong.	On Weak.	Running Out.	Total Hours.			

CEMENTS AND JOINTING MATERIALS.

1. **For Retort Lids.**—Clay joints faced with Portland cement.

2. **Soft Putty** for spigot and socket and other connections in contact with nitric acid vapour or liquid, hot or cold.

White asbestos flour	40 parts.	
Blue asbestos fibre	8 „	
China clay	10 „	
Tallow	2½ „	
Boiled linseed oil	21 „	(to make a stiff dough).

This putty can be made in quantity and stored, and old putty may be reincorporated. The fibre should be well teased by hand and got into the nature of fluff, otherwise hard lumps will appear in the finished mixture.

Mixing is best done in a mixing machine, so that the ingredients shall be thoroughly incorporated. An edge runner mill is found a better mixer than a kneading machine.

3. **Silicate Cement (Hard)**, for all kinds of permanent, inflexible jointings, and to serve as a cement-like top-coating for joints made with soft putty.

Coarse white asbestos powder.
Silicate of soda solution. S.G. 1·250 (approx.)

The ingredients are kneaded together to form a fairly stiff dough.

As this putty soon sets hard on exposure to the air, it should be mixed as required.

It is advisable to coat silicate cement joints with tar, especially where exposed to weather.

4. **Portland Cement**, for coating well-made joints where soft putty has been used—particularly serviceable for outdoor work.

5. **Rust Joint**, for retort lids and other permanent iron to iron connections.

Iron filings or borings, free from dirt and grease, and passed through a $\frac{1}{16}$-in. mesh sieve	5 lb.
Sal ammoniac	1 oz.
Sulphur flowers	2 oz.
Water	Sufficient to damp.

The ingredients are well mixed to give a mass just damp to the feel. This is then well tamped home by steel chisels to give a good firm joint.

6. **Joints for Acid-proof Brick Floors.**—

(*a*) *Anhydrous Tar* . .
Dried Powdered Fireclay } Mixed hot to give a workable plastic mass which sets hard on cooling.

In setting the bricks they are first warmed on a hot plate, dipped into the mass of fireclay and tar which is provided hot from an adjacent heating pot, and then laid with as little joint space as possible. Any joint space not filled in with the mixture has additional jointing material poured in and rubbed in by the use of a specially shaped iron which is heated as required.

(*b*) *Acid-resisting Cements*, for floors not subject to water:—
(i) Nori cement.
(ii) Chance and Hunt cement (patent specification for which is given on p. 242).

7. **Packing for Earthenware Block Cocks.**—These cocks are jointed to flanged pipes by using thin asbestos board washers which have been previously soaked for thirty minutes in boiling mineral jelly.

8. **Packing for Pump and Valve Glands.**—Blue asbestos cord of suitable diameter which has previously been soaked for thirty minutes in boiling mineral jelly.

9. **Jointing Material for Sulphuric Acid Pipe Lines.**—Asbestos millboard soaked in a strong solution of silicate of soda and applied wet.

10. **Patching of Cracked Earthenware.**—Asbestos woven cloth, soaked in a strong silicate of soda solution, is used.

If possible the cracked portion should be cleaned and washed with a solution of soda ash. A suitably sized piece of asbestos cloth, soaked in silicate of soda solution, is then fixed over the crack. If necessary it may be bound on with asbestos cord and finally painted over with silicate of soda solution.

Note.—While the above notes on jointing materials are by no means exhaustive, they are based on actual experience, and the materials have proved successful in long usage. No other jointing materials were found necessary on the nitric acid plant at H.M. Factory, Gretna.

Descriptions of Various Nitric Acid Plants and Processes kindly supplied from the Following Sources.

British Dyestuffs Corporation, Dalton Works

(*per* Dr. W. B Davidson).

During the War.

General.—The whole of the nitric acid was made in twenty 1-ton vertical retorts, working under the Valentiner vacuum system, and forty horizontal retorts working under chimney draught only.

Vertical Retorts.—During the war the Valentiner plant was worked two 12-hour shifts six days per week, that is 240 tons of nitrate per week. Since the armistice, however, they have only worked one shift per day, and I attach herewith a description of our present method of working.

A typical example of the record of the temperature given by a thermometer placed about 2 ft. through the top of the retort, when using 88 per cent. sulphuric acid, is as follows:—

Time.	Temp.	Time.	Temp.
8.0 A.M.	45° C.	1.0 P.M.	150° C
8.30 ,,	50 ,,	1.30 ,,	148 ,,
9.0 ,,	85 ,,	2.0 ,,	145 ,,
9.30 ,,	110 ,,	2.30 ,,	148 ,,
10.0 ,,	122 ,,	3.0 ,,	150 ,,
10.30 ,,	135 ,,	3.30 ,,	155 ,,
11.0 ,,	140 ,,	4.0 ,,	165 ,,
11.30 ,,	138 ,,	4.30 ,,	185 ,,
12.0 NOON	138 ,,	5.0 ,,	200 ,,
12.30 P.M.	145 ,,		

When using 88 per cent. sulphuric acid, a typical analysis of the nitric acid made is as follows:—

Specific gravity	1·464
Total acidity as HNO_3	80·81
HNO_2	0·64
H_2SO_4	0·06
HCl	0·01 to 0·04

Horizontal Retorts.—These retorts were coal-fired by hand, and were charged with 1200 lb. nitrate and worked off in thirteen to fourteen hours. The average efficiency was slightly higher than the Valentiner, being about 95 per cent.

The acid contained more nitrous acid than the Valentiner and averaged about 0·8 per cent.

The life of the retorts was only about 400 half-ton charges. This short life may be due to inferior castings.

CONDENSING SYSTEMS.—Both sets of plant have earthenware still heads and an earthenware 40-gall. jar to trap any entrained sulphuric acid. The gases are then divided into two streams and passed through 43 ft. of flanged 3-in. Narki air-cooled condensers, then through 84 ft. of 2-in. earthenware coils totally immersed in water. The two streams then unite and the acid which condenses is collected at this point in earthenware jars.

In the horizontal retort house the gases then join from ten units, and pass up three towers 3 ft. by 12 ft. packed with broken brick, and to the chimney. In the Valentiner plant the gases pass through a 66-ft. earthenware coil 2 in. diameter, immersed in water, then through seven small jars, the last three of which being partly filled with water before commencing each distillation. They then pass through an earthenware tower 2 ft. 6 in. diameter by 6 ft. deep and bubble through a seal of lime water 13 in. deep. A steam-driven vacuum pump draws the gases from this tower and passes them to the chimney.

Vertical Retort Plant, Method of Working 16th January 1919.—All the men and foremen start work at 8 A.M. They are divided into two gangs. One gang of labourers starts charging the nitrate into the retorts and the other gang of stillmen starts preparing the retorts for working.

CHARGING.—The previous afternoon the four charging skips have been filled and weighed with exactly 1 ton of nitrate of soda and left standing in the nitrate stores. The hard nitrate has also been broken up and made easy for shovelling. This enables a good start to be made in the morning.

The nitrate is shovelled into a tared skip, 1 ton weighed in, hoisted to the level of the retort tops, pushed along the overhead runway from the stores to the vertical house, and tipped by hand down a shoot into the open retort. No. 1 retort (the farthest from the stores) is filled first, then Nos. 11, 2, 12, 3, etc., until the whole twenty retorts are charged. This operation takes one to one and a quarter hours.

The charge-hand of each ten retorts turns on gently and lights the producer gas under each retort at 8 A.M.

While the charging is proceeding, the stillmen and other process men clay and stop up the tapping off outlet, fill the three final jars with water, and clean the retort lids. They clay down the joints as soon as the retorts are charged.

Two men and the mechanic get the pumps ready for starting. The pump-man fills the guard tower on the pump inlet with lime water, oils and warms up the pumps, and finally starts them.

As soon as a retort is charged, its lid fixed down and a vacuum of 4 to 5 lb. per square inch is registered on the pump inlet, the sulphuric acid is drawn into the retort from a C.I. measuring tank. About 1·1 tons 90 per cent. H_2SO_4 are run in, and an exact quantity is measured off to give a nitre cake of 28 to 29 per cent. free H_2SO_4. When the acid is run in, the gas burners are turned on nearly full.

The above operations are usually completed about 9.15 A.M., but any delay through an acid pipe being blocked or a pump requiring attention throws the starting time of distillation later.

DISTILLATION.—The gas is kept full on for about an hour until nitric acid appears in the sight glass after the first set of cooling coils. The temperature in the top of the retort is then about 120° C. The gas has now to be reduced and regulated to give an even flow from the cooling coils. If the gas is turned on too high the distillation will be violent and oxides of nitrogen will be formed, which will cause a pressure in the retort which may blow off the lid. The stillman has to regulate the gas so that the maximum speed is obtained without blowing the joints of the retort. From 10.30 A.M. to 2 P.M. the temperature fluctuates between 120° and 140° C.

The receiving-jars are changed over and four carboys of acid are drawn off from the jars into the carboys at 12 noon, 2 P.M., and 4 P.M. The strongest acid of 104° Tw. is drawn off first. Towards the end of the distillation the acid made is only 70° Tw.

After 2 P.M. the gas is increased and the temperature brought up to 200° C., at which point the distillation ought to be complete; this normally occurs at 4.30 to 5 P.M. If the temperature is raised too rapidly at this period the charge is liable to boil over.

When 200° C. is reached, the gas is turned out and the retort left to stand for half an hour, so that the pump can draw off the acid fumes from the system.

When the pump is stopped and the nitre cake run into the cast-iron pans, the retorts are raked out and the run-off holes are cleaned ready for next morning. Meanwhile the rest of the acid made (about three carboys per still) has been drawn off from the jars into carboys.

The nitre cake is left to cool and set all night. It is broken up and loaded into wagons by the charging gang after they have finished charging the retorts next day.

The total period of distillation from the time of running in the sulphuric acid to tapping off the nitre cake is normally eight hours. This, together with charging (one hour), running in sulphuric acid (quarter of an hour), and tapping off the nitre cake and finishing (three-quarters of an hour), makes the operation complete in ten working hours; but any delays such as those due to leaking pottery or condensing pipes, pump trouble, or a boil over prolong the time. Also any stoppage of the continuity of the process caused by the stillmen leaving the plant for a fixed dinner hour, causes a prolonged period of distillation.

The acid is run into carboys and handed over to the mixing-plant staff to weigh, test, blend, blow clean if required. It is then stoppered and loaded or mixed with sulphuric acid for mixed acid.

YIELD.—About fifteen carboys of nitric acid are produced per retort. The total weight is about 2000 lb. of an average strength of 91° Tw. when using 162° Tw. sulphuric acid. This equals about 1550 lb. 100 per cent. nitric acid. The average efficiency for the period 1st August to 31st October 1918 was 94·5 per cent. of 100 per cent. nitric acid produced from the weight of nitrate charged.

About 1·15 tons of nitre cake are produced per retort. The average ratio of the weight of 100 per cent. sulphuric acid used to the actual weight of nitrate charged for the period 1st August to 31st October 1918 was 0·933 : 1.

The average life of retorts fired by producer-gas is 1100 one-ton charges.

Mr W. C. Wakefield, Chemical Manufacturer, Dewsbury.

It was difficult in the early days of the war to secure orthodox plant for this work, and I therefore decided to use such materials as I could conveniently procure for the erection of plant capable of decomposing about 120 tons of nitrate of soda per week.

The stills are ordinary decomposing pans such as are used in the saltcake process. They are 10 ft. 6 in. in diameter and 2 ft. 6 in. deep. They were supplied by the Widnes Foundry Co., Ltd., and have done very good work. Already they have decomposed about 1300 tons of nitrate of soda each, and are still in good condition. They were set in in the ordinary way and covered by a brickwork dome set in ground mortar, with a little cement added (see Fig. 76, p. 134).

In the first instance the condensing plant was composed of 12-in. earthenware drain pipes built in columns 9 ft. high, each column standing on a stone base 20 in. square. The stones were hollowed and fitted with a glass syphon to deliver the acid into the carboys. There were sixteen columns in each battery of pipes, and following these were two wash-out jars of 50-gall. capacity fitted with perforated dip pipes. The plant was draughted by an earthenware steam-jet worked at 50 lb. pressure. The residual gases which contained very little nitric acid were delivered to the chimney flue. The condensed water from the jets was caught (on its way to the flue) in a bath and used to charge the wash-out jars.

The process was worked as follows: After charging the end wash-out jar with water, and first one with weak acid about 15° Tw. (which had during the previous charge served for the end jar), a charge of 18 cwt. nitrate of soda was thrown into the still and evenly levelled down.

The charging door was put on and pointed round with mortar, and the requisite quantity of sulphuric acid run on. During the charging the fire was always kept very low, only so much being left on the bars as would serve to light off again. Decomposition began at once, and condensation could be noted by the runs into each carboy standing before the battery. As

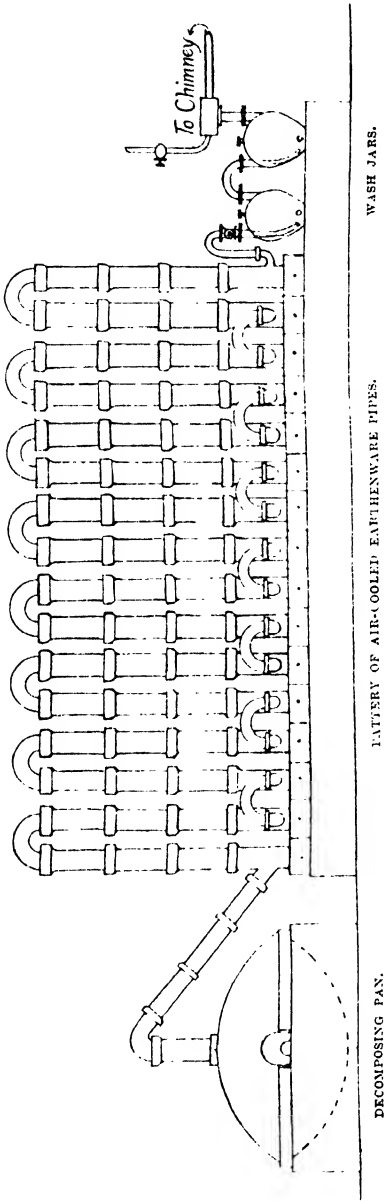


FIG. 76.—Wakefield's Air-Cooled Nitric Acid Plant.

soon as the runs began to slacken the fire was remade, being kept low during the first three hours, afterwards raised briskly and continued to the finish six to eight hours after charging. The finishing point was ascertained by pushing a rod into the charge and noting condition of the adhering nitre cake. Each charge of nitre cake was tested for H_2SO_4 and HNO_3. Almost invariably the latter amounted to no more than a trace and the former 28 per cent.

The nitre cake was pushed from the still on to a large cooling floor holding about 200 tons and was removed periodically. The pushing was effected by a specially constructed box pivoted on to the shank so as to conform to the curvature of the pot. The charge could be pushed in from ten to fifteen minutes.

The carboys of nitric acid were removed as filled and mixed off to the required strength. The acid in the wash-out jars generally rose to about 60° Tw. in the first and 15° Tw. in the end one. That at 60° was used to reduce the main portion of the charge.

The still could at once be recharged and the process repeated.

You will notice that the time of working is stated as from six to eight hours, but this depended on the goodwill of the men. Some times even shorter time was required; but such quick working put a great strain on the condensing plant and caused much sweating through the pipes, and sometimes pipes would crack. The cracks were then patched with asbestos and silicate cement, and so the plant continued to work for over twelve months with good results.

Later on the whole plant was renewed on the lines shown in Fig. 77, one still being done at a time. The first eight columns were removed altogether, and were replaced by Hough's Narki condensers and batteries of 6-in. silica ware S-pipes all water-cooled. The remaining eight columns were placed in earthenware baths and continued to work with little change in working conditions. It was, however, now found that the charges could be worked off somewhat quicker than

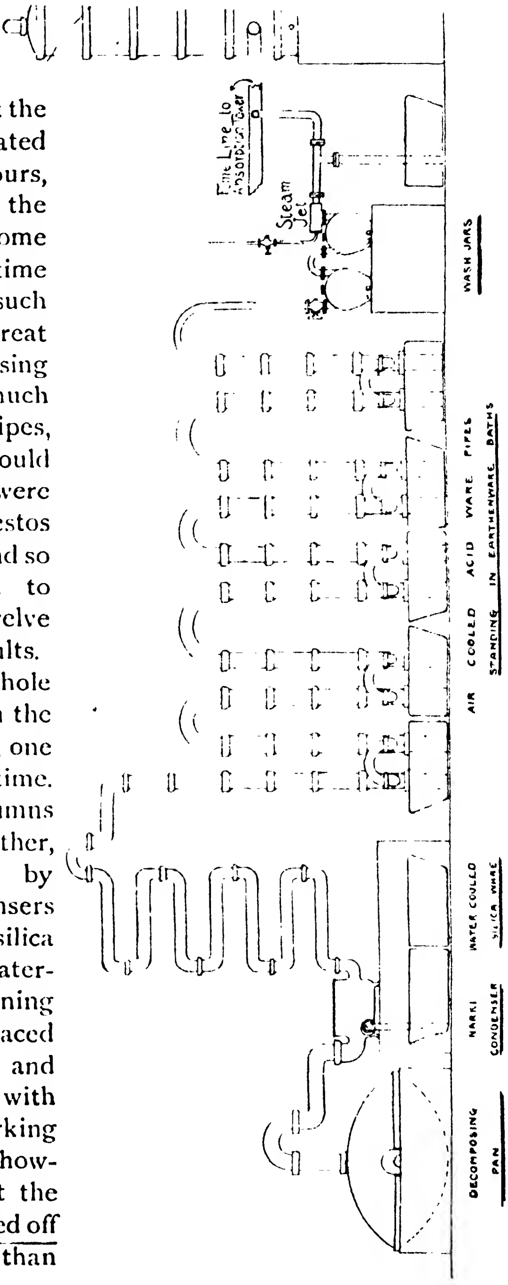


FIG. 77.—Plant as modified in 1916 and 1917.

formerly without so much cracking of plant, as most of the heat was removed in the water-cooled portion of the plant. The wash-out jars continued to work much as under former conditions.

South Metropolitan Gas Company

(*per* P. Parrish, A.I.C.).

Nitrate of Soda.—In order to ensure high yields, it has been found necessary to exercise great care in the sampling of all consignments of nitrate of soda delivered.

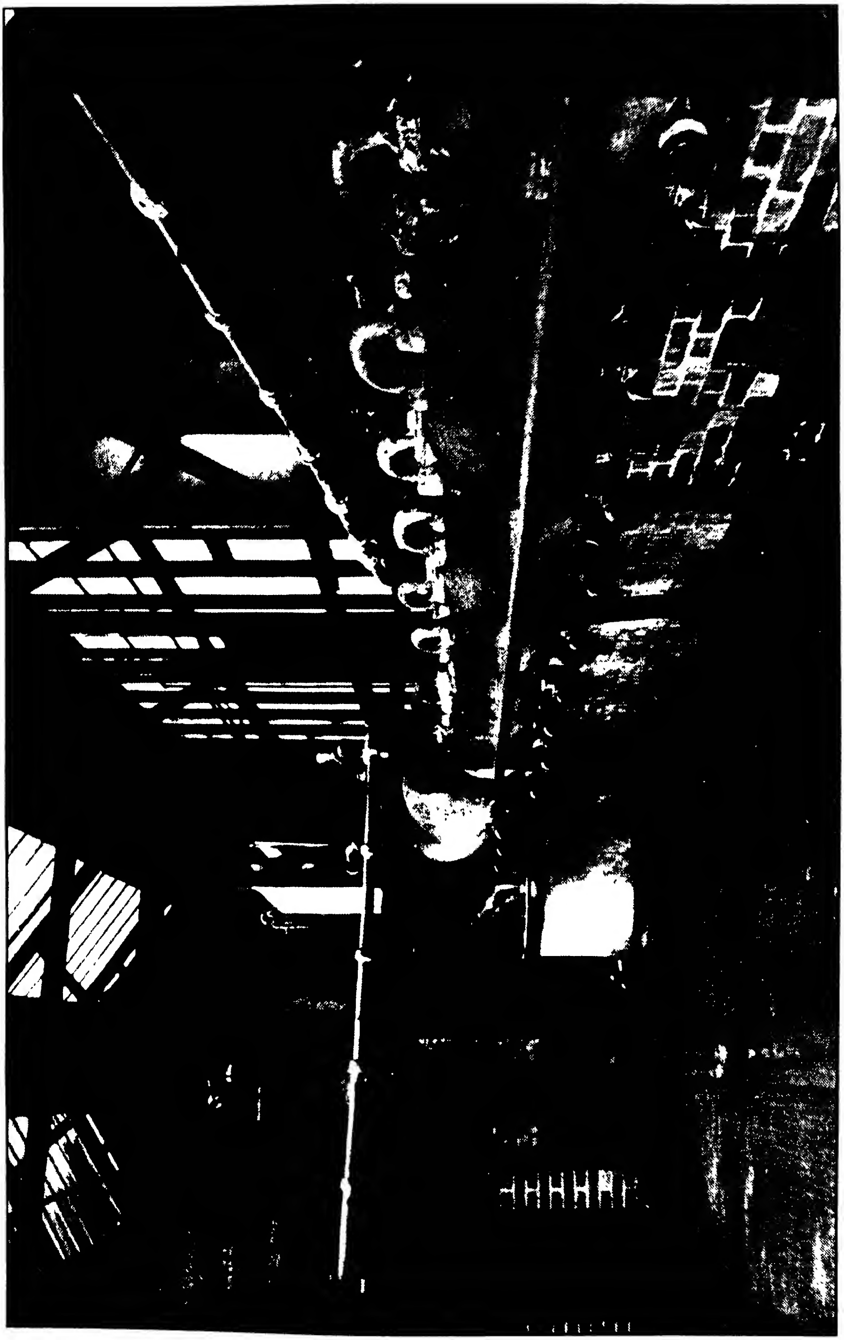
The method which is usually pursued of piercing bags and drawing a sample with an auger tube does not give an absolutely representative sample. The tube does not pierce the full depth of the bag, and its cross section is relatively small compared with the cross section of the bags being sampled. Further, the mode of sampling does not reflect the quality of the lumpy nitrate of soda, which was not uncommon in many of the consignments received during the war.

It has been found necessary in the case of 100-ton consignments to take one bag in every ten, empty the contents, and adopt the usual quartering method. With smaller consignments, of (say) 20 tons, it has been our practice to take one bag in every five.

General.—The South Metropolitan Gas Company's Valentiner nitric acid plant comprises one 20-cwt. still and one 15-cwt. still worked with one Clabour vacuum pump.

Operation of Plant.—It has been found necessary with the Valentiner type of nitric acid plant to allow twelve to thirteen hours for the working of a ton charge, and two hours for cooling prior to the still being recharged with nitrate of soda.

After charging the still with the quantum of nitrate of soda, the man-lid is secured. The acid feed is commenced, and having ensured that all the Woulff's jars are in a satisfactory condition, the vacuum engine is run slowly for a time. A small fire is then placed under the still. It has been found desirable to occupy about half an hour in running the acid into the still. After this has been effected, the vacuum engine is run more quickly and the fire increased. Operating under a reduced pressure of 10·7 lb. per square inch absolute, there has invariably been a tolerable flow of nitric acid on the outlet



[*Face page* 136.

of the cooling worms two hours after charging, and this rate of flow has been maintained for at least five hours. It has been usual to collect the nitric acid in the first 50-gall. jar during the initial three hours. This jar is then put out of action, and No. 2 connected. To obviate any possibility of fracture of the mixing vessels, it is usual to leave the acid to cool for four or five hours, and acid is never drawn from either of the jars, or the mixing pan, at a higher temperature than 36° C. All the 50-gall. jars are drawn off prior to the restarting of the plant, as also the protecting jar. The nitre cake is tapped off from the still about forty minutes after the completion of the distillation. Immediately prior to this, the vacuum on the still is decreased appreciably and the temperature raised in order to increase the fluidity of the nitre cake. The acid is drawn forward from the 20-gall. back jars for concentration, and weak acid from the towers used in those which have been emptied. Working continuously in this way for five years, it has not been found necessary to replace a single still.

With the Valentiner type of nitric acid plant, it is possible to produce either 80° Tw. (65 per cent. HNO_3), 84° Tw. (70 per cent. HNO_3), or part 100° Tw. (94 per cent. HNO_3), and part 84° Tw. nitric acid at will, with slight modification in the method of working. For the production of the higher strength acid it has not been found necessary to resort to the drying of the nitrate of soda, provided sulphuric acid of 96 per cent. strength is used, and the back jars are worked judiciously with a view to securing maximum nitric acid concentration. Operating in this way, 55 per cent. of the make of nitric acid would be 100° Tw. and the balance 84° Tw. The content of hyponitric acid can be maintained at 0·25 per cent., by introducing a small but continuous supply of air through the nitric acid as collection is effected in the 50-gall. receivers.

Chemical Engineering Notes.—The Clabour type of vacuum pump embraces a lignum vitæ piston block, phosphor bronze liner, phosphor bronze piston rod, lignum vitæ valve seats, and india-rubber ball valves—suction and delivery.

The pump, which is of the wet type, should withdraw through the cylinder a continuous steady stream of a weak solution of soda ash, and as this solution is discharged to a tank, and kept in cycle for a time, it is important to see that no dust or gritty matter reaches the solution in question, otherwise "scoring" of the liner and gland may arise. It is advisable to discard the circulating solution immediately it shows the slightest sign of acidity. The discarded solution consists of a weak solution of sodium nitrate and sodium nitrite.

It has been found that the best packing for the gland is one of india-rubber and graphite.

If mechanical troubles are to be obviated, it is essential to provide adequate cooling surface in the shape of twenty-four 20-gall. receivers, in addition to four sets of cooling worms, for a plant of the size under review. Each alternate receiver should be provided with a dip arm so as to ensure definite bubbling of the gaseous nitric acid through weak nitric acid or water.

To ensure reasonable life of the cooling coils, it has been found advisable to wrap the first three or four rings with calico dipped in a slurry of silicate of soda solution and asbestos. Water-spraying of the coils in lieu of immersion has been found to add considerably to the life of this portion of the plant.

The United Alkali Company.

Nitrate Nitric Acid Plant.—Our nitric acid plant consists of a number of stills each capable of holding a charge of sodium nitrate weighing 3 tons and heated underneath by a small coal fire. The stills are vertical and are raised about 4 ft. above ground-level, allowing the nitre cake to be run into cast-iron trays standing at a convenient level for discharging the contents when cold into wagons.

Arsenical sulphuric acid of 168° Tw. (94 per cent. H_2SO_4) is used for the distillation, and 95° to 100° Tw. nitric acid (84 to 94 per cent. HNO_3) obtained. When working for 80° Tw. nitric acid (65 per cent. HNO_3), a weaker sulphuric acid of 148° Tw. (78 to 80 per cent. H_2SO_4) is used.

The nitric acid vapours leaving the top of the still pass through a number of silica S-bends about 8 in. diameter, sloping downwards to a silica coil immersed in water and luted with nitric acid.

The uncondensed vapours rise from a special silica vessel

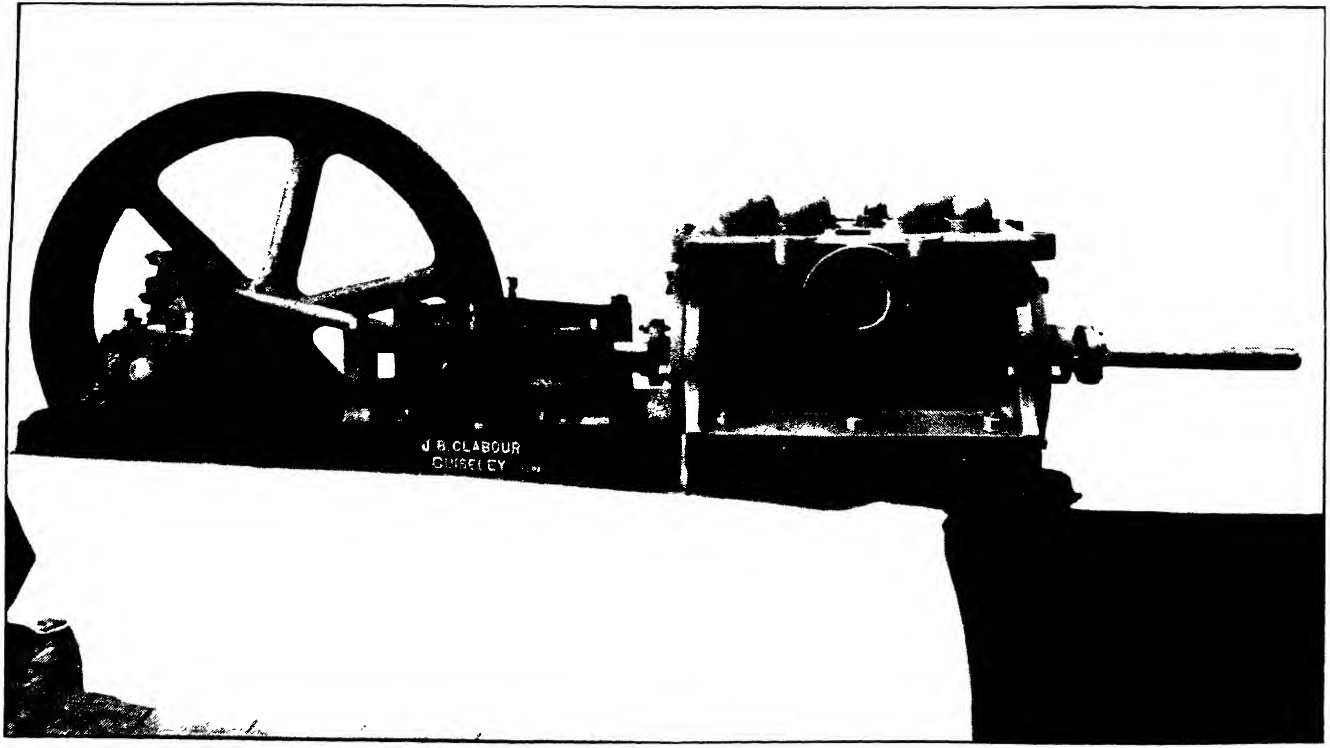


FIG. 79.—Clabour Vacuum Pump, showing Ball Valves. (J. B. Clabour, Guiseley, Yorkshire.)

[*Face page* 138.

above the coil with four branches and pass through four rows of S-bends 6 ft. 6 in. long by 4 in. diameter, each row having seven of these bends. Water is circulated over these coils and the condensed acid runs back to the acid cooler.

This condensing apparatus is designed by the Thermal Syndicate, Limited, Wallsend-on-Tyne.

Following the coolers, the gases pass through a series of earthenware towers, 3 ft. diameter and about 17 ft. high. The tower sections are each 3 ft. high, and each contains a perforated earthenware plate which carries earthenware rings and packers. Acid is circulated round the towers by means of earthenware air lifts and glass pipes about 1 in. diameter. About 10 per cent. of the total acid recovered is obtained in the towers at about 85° Tw. (70 per cent. HNO_3). Behind the nitric acid towers, as a final wash, are two towers with circulating vitriol at 168° Tw. which afterwards feeds the stills. The draught is obtained by means of a "Sirocco" fan, electrically driven, forcing an air current through an earthenware ejector. This fan gives 3 in. water pull at the fan and about ½ in. pull on the top of the still.

It will be noticed that no acid gases pass through the fan.

We have tried earthenware and special cast-iron fans for creating a direct draught, but owing to their liability to burst while running at a high speed we have had to discontinue their use.

ELEVATION OF NITRIC ACID AT THE TOWERS.—We used a stoneware "Montejus" operated by compressed air and delivering through stoneware pipes. Owing to the danger of joints bursting out if acid reached the holding bolts of the joint clamps we did not feel safe and discontinued its use.

We tried an earthenware centrifugal pump but could not keep the gland tight and acid leaked on to the base of the pump. If this had been successful there would still have remained the danger of joints noted above.

The air lift elevator has been quite successful but requires a large volume of air in comparison to the amount of acid raised.

Another apparatus which we have tried experimentally only, and which looks promising, is the "Dawson Spray."[1] The acid in the base of an empty tower is atomised by a jet

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[1] Dawson, B.P. 120869, 1918 (see p. 218).

of air and carried upward in the current of gas in the form of a mist. There is intimate contact between the acid and the gas, and the cost of packing the towers is eliminated.

WORKING OF STILLS.—After running off the previous charge of nitre cake, the still is allowed to cool for about an hour with the charging lid off. A 3-ton charge of nitre is dropped in, the lid sealed with clay, and the vitriol run in, taking about half an hour. A small fire is put to the still and the acid begins distilling over. Care must be taken at this stage to prevent the still becoming too hot as the nitre is not thoroughly mixed with the vitriol, some being above the vitriol level. This coned-up nitre becomes "undermined" and falls into the liquid, which, if too hot, causes a sudden evolution of nitric acid which cannot be coped with even when a good draught is maintained. A sudden "blow" causes considerable loss of nitric acid, the heavy earthenware lid at times being lifted bodily from the charging hole.

About eighteen hours after first applying heat, the contents of the still are stirred up with an iron rod, and from the condition of the bisulphate adhering to the rod, the experienced process man is able to gauge the time necessary to complete the finishing of the charge. The firing now must be increased to drive off the last traces of HNO_3 and to render the nitre cake more fluid.

The average time taken to distil a 3-ton charge of nitre is about twenty-four hours. The temperature of the nitre cake running out of the still is in the neighbourhood of 340° F.

The clay stopper at the bottom of the still is broken out and the nitre cake run on to cooling trays to a depth of 3 to 4 in. When cool it is broken up into pieces and loaded into wagons for use in other departments or for sale.

Each charge of nitre cake is tested and contains a trace of $NaNO_3$ and 26 to 28 per cent. total acidity as H_2SO_4.

YIELD.—When making concentrated nitric acid (95 to 100° Tw.), a yield of 95 to 96 per cent. is obtainable with a consumption of—

9 to 10 cwts. fuel per ton 80° Tw. nitric acid.
20 to 21 cwts. 168° Tw. sulphuric acid per ton.

When using 148° Tw. sulphuric acid for 80° Tw. nitric acid, the yield is slightly greater.

CONVEYANCE OF NITRIC ACID.—Concentrated nitric acid of 95 to 100° Tw. for use in other departments is carried in cast-iron containers mounted on railway wagons, a fully loaded wagon holding 6 tons.

For sale, nitric acid is packed in glass carboys holding about 1¼ cwt. each. Clay or earthenware stoppers are sealed on with plaster of Paris, and covered over with a piece of sacking.

Saint Martin de Crau Works of the Société Anonyme d'Explosifs et de Produits Chimiques

(*per* MONSIEUR C. HOMÈRE, Manager).

The Valentiner plant is used and is found very satisfactory. Condensation is effected in earthenware coils and bottles as in the original design. The uncondensed nitrous gases passing the condensing system are absorbed in a solution of caustic soda.

Some works have replaced the earthenware runs from the retorts and the earthenware coils by acid-resisting irons, using simple S-pipe condensers.

The average time of a good distillation is nine hours, but to avoid frothing and loss of HNO_3 it is considered advisable to exceed this rather than fall below it.

The nitre is not dried, though in many factories drying is effected by means of the waste heat from the flues heating the retort.

Concentrated sulphuric acid of 92 to 94 per cent. H_2SO_4 is used to decompose the nitre, and this allows the inclusion in the charge of a small quantity of weak nitric acid from a previous distillation.

Brotherton & Co., Leeds

(*per* E. S. WHITELOCK).

Nitric Acid Plants.—We used the 2-ton C.I. pot type of still, hand-fired in some cases, but principally fired by producer-gas.

After experience with the Guttmann, Hart, and Valentiner types of condensing batteries, we finally adopted the silica condensers made by the Thermal Syndicate, using Narki metal pipes for the first two pipes from the still.

The strength of acid made was 65 per cent. HNO_3.

The fumes leaving the condensing batteries were finally dealt with in 30-in. stoneware towers, eight towers to four stills, packed with acid-resisting Nori rings and having continuous circulation by means of stoneware and glass air-lifts.

The draught in the towers was produced by steam ejectors of stoneware with silica steam nozzles. Whilst admittedly somewhat expensive in steam, they were in the long run more satisfactory than the various types of fans tried.

Storage of the finished acid was in large stoneware tanks suitably vented into the fume main. Storage of 65 per cent. nitric acid in aluminium tanks was not satisfactory, owing to action on the surface level, presumably due to dilution of the acid by moisture in the atmosphere.

Nitre cake was dealt with in the usual manner in 8 ft. square shallow cast-iron pans.

For 65 per cent. acid it was not found necessary to dry or grind the sodium nitrate.

Sulphuric acid (B.O.V.) was received at the works in tank wagons, run into stores below rail level, and elevated from there to a measuring tank placed above the stills. The measured charge was then run to a supply tank for each still.

DEVELOPMENTS IN N/A MANUFACTURE IN THE U.S.A. SINCE 1914.[1]

"The building of the new nitrate of soda acid plants has offered an excellent opportunity for the introduction of many improvements. The Dutch ovens under the retorts have been displaced by modern fire-boxes provided with a proper arch. This change has effected a saving in coal consumption of approximately 25 per cent. The chemical stoneware from the retorts to the condensers and the glass condenser tubes have been replaced by acid-proof, high silicon iron, such as Duriron and Tantiron. The volvic-ware saucers in the towers have also been displaced by acid-proof iron. The chemical stoneware from the condensers to the absorption towers, and the glass lines for circulation of acid at the sides and top of the towers, however, are retained. The absorption tower capacity has been increased about 40 per cent. by the addition of more towers.

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[1] Pranke, *J. Ind. Eng. Chem.*, 1918, 10, 830-31.

Spiral rings for tower packings have taken the place of the ordinary form of packing.

"Important changes have also been made in operation. The average charge of 5000 lb. of nitrate per retort has been increased to about 7500 lb. The retorts, instead of being operated in batches, are operated in rotation. Instead of three runs per retort per day, the usual practice is now two runs per day. Temperatures are also controlled more carefully than in the past.

"The result of these improvements is an increase in the amount of nitrogen recovered as acid from an average of about 78 to 80 per cent. to about 92 to 94 per cent. of the nitrogen in the nitrate of soda. At the same time the labour requirement has been somewhat decreased."

WORKING RESULTS OF NITRIC ACID PLANTS.

Typical manufacturing results are shown in the accompanying reports of various H.M. Factories, where very careful records of all processes were kept :—

H.M. FACTORY, GREETLAND.

Week ending 6 A.M., 27th July 1918.

Nitric Acid Manufacture Report.

EFFICIENCY.

HNO_3 Equivalent to Crude Nitrate consumed (1) at Retorts, 68·65 tons ;
(2) Overall, 69·95 ,,
HNO_3 produced at Retorts, 66·12 tons.
Loss of HNO_3 (1) at Retorts, 2·53 tons ; (2) Overall, 3·83 tons.
Percentage loss (1) ,, 3·71 per cent. ; (2) ,, 5·47 per cent.
Efficiency at Retorts = 96·29 per cent.

Number of Retorts charged, 65 ; tapped, 65 ; average time of cycle, 24·4 hours.
Fuel consumed, 22·75 tons = 0·34 ton per ton HNO_3 produced.

Average Acidity of Nitre Cake, 30·08 per cent.
H_2SO_4 consumed (*a*) per ton $NaNO_3$, 0·96 ton ; (*b*) per ton HNO_3, 1·34 ton.
Theoretical Acidity of Nitre Cake, based on H_2SO_4 Usage, 30·0 per cent.

REMARKS :—

(Signed) ....
Chemist in Charge.

H.M. FACTORY, PEMBREY.

Week ending 6 A.M., 2nd February 1918.

Nitric Acid Report. (*N.C.*).

SHEET A 1. RETORTS.

Number of Retorts working	14	Number of Charges made during week		101
Charge per Retort	2·634 tons	Dry Nitrate, $NaNO_3$		97·3 per cent.
	2·600 "	Sulphuric Acid, H_2SO_4		92·50 "

MATERIAL CONSUMED.

Dry Nitrate	266·0 tons	Equivalent to $NaNO_3$		258·8 tons
		HNO_3		191·8 "
Sulphuric Acid	262·6 tons	H_2SO_4	92·50 per cent.	242·9 "
Fuel consumed—(*a*) in Drying	3·2 "			
(*b*) at Retorts	30·3 "	= 0·18 ton per ton HNO_3 produced.		

MATERIAL PRODUCED.

Strong Nitric Acid	178·4 tons	HNO_3	89·0 per cent.	158·8 tons
Weak Nitric Acid	37·1 "	HNO_3	62·3 "	23·1 "
Nitre Cake produced	324·5 "	Acidity as H_2SO_4		28·50 per cent.

HNO_3 LOST.

HNO_3 Equivalent to Nitrate Charge to Retorts	191·8 tons
HNO_3 produced	181·9 "

HNO_3 lost 9·9 tons . 5·2 per cent. on HNO_3 Equivalent to Nitrate charged.

REMARKS :—

(Signed)..

6th February 1918.

H.M. FACTORY, CRAIGLEITH.

Week ending 12 noon, 29th June 1918.

Nitric Acid Report.

SHEET B 1.

(Quantities as Tons of 2240 lb.)

Number of Retorts working	5	Retorts charged during week	30
Retorts tapped during week	30		

CHARGED TO RETORTS.

Nitrate of Soda	82·5 tons ; equivalent to pure $NaNO_3$		77·55 tons
	HNO_3		57·48 "
Sulphuric Acid	85·72 tons	H_2SO_4 93 per cent.	79·72 "
Fuel consumed	... "		

PRODUCED.

Strong Acid	54·44 tons	HNO_3 93 per cent.	50·63 "
Weak Acid	5·66 "	HNO_3 60 "	3·40 "
Nitre Cake	100 tons ; Average Acidity	29 per cent. H_2SO_4	

EFFICIENCY.

HNO_3 charged as $NaNO_3$	57·48 tons	
Total HNO_3 produced	54·03 „	
	Loss = 3·45 „	= 6 per cent. on HNO_3 Charged as $NaNO_3$

REMARKS :—

Crude Nitre contains 94·7 per cent. Sodium Nitrate.
„ „ 0·7 „ „ Chloride.

(Signed)...

Chemist in Charge.

H.M. FACTORY, GRETNA.

Monthly Report, five weeks ending 7.30 A.M., 2nd March 1918.

Nitric Acid Retorts.

Total Number of Retorts charged	138¼ Wet 1359¾ Dry	1498
„ „ „ tapped		1505

CHARGED.

	Tons		Per cent.		Tons
Sodium Nitrate—					
Amount Wet	276·5	$NaNO_3$	96·6	HNO_3	197·97
Amount Dry	2719·5		98·41		1983·58
Sulphuric Acid—					
Amount	3095·52	H_2SO_4	92·0	H_2SO_4	2849·44
Coal used in Producers	401·54				

PRODUCED.

Nitric Acid—	Tons		Per cent.		Tons
Amount, Strong	1986·07	HNO_3	92·4	HNO_3	1835·62
Amount, Weak	380·19	HNO_3	63·75	HNO_3	242·38
Ex. Towers	106·67	HNO_3	59·7	HNO_3	63·67
				Total	2141·67

LOSS.

Nitric Acid—

Total HNO_3 charged to Plant as $NaNO_3$	2181·55 tons
„ „ recovered as HNO_3	2120·96 „

Amount lost, 60·59 tons = 2·78 per cent.

PHYSICAL DATA.

Time of Distillation	11 hours, 43 minutes
„ Cycle (charging to re-charging)	14 „ 48 „
Nitre Cake—	
Percentage free H_2SO_4	28·43
Fuel—	
Coal used per ton of Acid recovered	0·16 ton
„ „ „ HNO_3 „	0·19 „
Nitric Acid—	
Average Strength of Acid recovered	86·6 per cent.
Tons produced per Retort	1·6
Percentage recovered as Strong Acid	85·7 per cent.
„ „ Weak Acid	11·3 „
„ of Weak Acid recovered in Towers	3·0 „
Total Recovery	97·22 „

Note.—Seven retorts in process at commencement of monthly period.

H.M. FACTORY, GRETNA.

Nitric Acid Retorts.

	Six Months ended 30th June 1917.	Six Months ended 29th December 1917.	Six Months ended 29th June 1918.	From Start-up of Plant to Final Close-down, 7th June 1919.
Total Crude Nitre consumed (Wet) .	10783·93 tons	12739·11 tons	12766·24 tons	49527·23 tons
Charged in as { Wet	4470·19 ,,	1674·0 ,,	740·5 ,,	11028·14 ,,
Charged in as { Dry	6205·16 ,,	10850·9 ,,	11805·0 ,,	37795·06 ,,
Net HNO_3 produced	7206·82 ,,	8612·91 ,,	8787·47 ,,	33502·61 ,,
Efficiency	94·68 per cent.	94·98 per cent.	96·36 per cent.	95·47 per cent.
Average Strength of Nitric Acid produced	86·11 ,,	85·53 ,,	86·5 ,,	86·46 ,,
H_2SO_4 per ton HNO_3 produced . .	1·456 tons	1·397 tons	1·354 tons	1·395 tons
Crude Nitre per ton HNO_3 produced .	1·496 ,,	1·479 ,,	1·453 ,,	1·478 ,,
Coal consumed per ton HNO_3 produced .	0·250 ,,	0·260 ,,	0·215 ,,	0·250 ,,
Acidity of Nitre Cake (by analysis) .	31·8 per cent.	29·5 per cent.	28·74 per cent.	No analysis supplied for early period
Time of Cycle (charging to re-charging)	12 hours	13 hours, 7 minutes	14 hours, 55 minutes	14 hours, 3 minutes

CONTINUOUS PROCESSES.

Prentice.

In 1893 Prentice[1] introduced a continuous process for the production of nitric acid. He supplied nitrate of soda through a hopper to a small horizontal pug-mill, where it was mixed with the requisite amount of concentrated sulphuric acid. From the mixing mill the charge was delivered to a horizontal retort of rectangular section built in the flue of a coal fire. The retort had baffle partitions stretching from the cover but not reaching to the bottom. During working these baffles served to separate the retort into separate chambers, but the liquid mass in the retort could flow forward from chamber to chamber. Each chamber was provided at the top with a vapour pipe to conduct away the nitric acid. The full heat of the fire came under the compartment farthest removed from the charging end, and here the last of the nitric acid was removed before the nitre cake was discharged.

As the charge entered the retort it became decomposed, and the decomposition continued with increasing temperature as this portion of the contents of the retort moved progressively forward to make room for fresh additions and finally to take the place of nitre cake removed at the discharge end.

Excess of sulphuric acid was used in order to ensure a free-flowing nitre cake, and this was utilised afterwards for the manufacture of superphosphate.

Prentice claimed a fuel saving of 66 per cent. in comparison with his plant working the discontinuous process. A continuous retort weighing 2 tons produced as much nitric acid (4 tons) per week as did two discontinuous retorts each weighing 5 tons.

In addition to economy in fuel consumption, a continuous process would entail a much less wear and tear on the retort, on the combustion chamber, and on the condensing system, as working conditions could be kept fairly uniform over long periods. The alternate heating and cooling involved in the discontinuous process is detrimental to the life of the retort, to the containing structure, and to the condensing system.

Prentice's process did not find favour and was never worked to any extent.

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[1] *J. Soc. Chem. Ind.*, 1894, **13**, 323.

Uebel.

More recently Uebel[1] introduced a continuous process involving the use of three retorts, two of which are built in the flue system carrying waste gases from the third retort which is at a lower level, and which receives the first heat of the furnace provided for the system.

While not quite eliminating the necessity for cooling during the admission of the charge, the Uebel process does to a large extent get over the great drawback of the discontinuous process due to alternate heating and cooling.

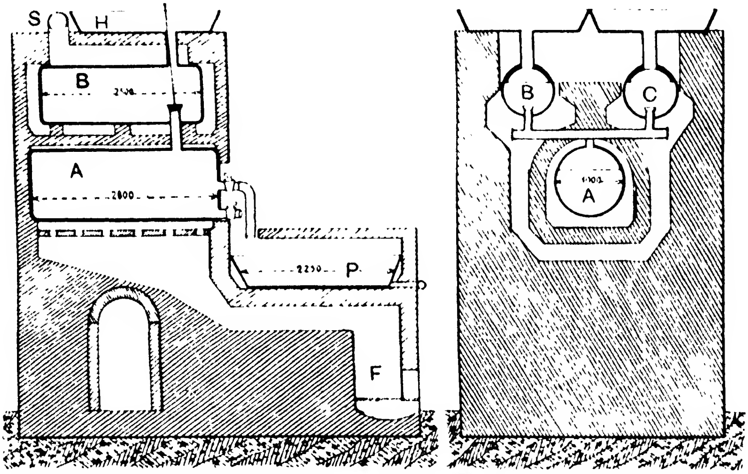

FIG. 80.—Diagrammatic Representation of Uebel Retorts.

The two upper retorts, B, C (Fig. 80), are alternatively charged with nitrate of soda and sulphuric acid, where the decomposition of which is only partially effected before transference to the lower and hotter retort A. For a period before retort A is due to receive a charge from B or C, nitre cake is discharged from it through an opening, the height of which allows only a determined quantity to flow from the retort.

Consider the process actually at work. The hot flue gases from retort A are by-passed round retort B which has just received a charge of nitrate and sulphuric acid. Retort C is meanwhile lying empty with no hot flue gases circulating

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[1] B.P. 19881, 1913 (see p. 214).

round it. Retort A has recently received the charge from C. Before the time for the transference of the charge from B to A, a quantity of nitre cake is discharged from the latter, and during discharge the heat of the furnace is modified somewhat in order to prevent a too violent reaction when the charge from B is transferred to A. On transferring the partially completed charge from B to A the flue gases are now by-passed from retort B to C which has been recently charged with nitrate and sulphuric acid.

At the time of discharge from a top retort the reacting material has reached a temperature of 170° to 200° C. In the lower retort the temperature of the melt varies from 250° to 300°.

Working Results:—

Total recovery = 95 to 96 per cent of Theory.
Average strength = 90 per cent. HNO_3.
Nitrous content = less than 0.15 per cent. (as NO_2).
Fuel consumption = 15 per cent. of the weight of nitrate.
Acidity of nitre cake = 37 to 38 per cent. H_2SO_4.
Ratio $H_2SO_4 : NaNO_3$ used = 1.05 : 1.

Points in Procedure.—1. The use of polysulphate, as designed in the original Uebel process, may or may not be resorted to, as desired.

Lunge,[1] in this connection, says: "The nitre cake, running out at a high temperature from the retorts, is mixed with sulphuric acid of about 1·71 sp. gr. in such proportions that a 'polysulphate' is formed, the water being evaporated by the heat remaining in the nitre cake. This polysulphate, of the composition $NaH_3(SO_4)_2$, serves instead of fresh sulphuric acid for manufacturing the next batch of nitric acid." Maugé[2] describes a strong heating of a portion of the nitre cake run from the bottom retort, "and the polysulphate so formed is returned to the top retorts." It is added at a temperature of 120° to 150° very slowly after the nitrate has been introduced. Sulphuric acid is added after the "polysulphate."

2. Shallow pans on top of the retort settings may be used for drying the nitre.

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[1] *Sulphuric Acid and Alkali*, vol. i., part 1, 4th ed., p. 154.

[2] *L'Industrie Chimique*, August 1920, p. 265.

3. At each discharge from the top to the bottom retort, a portion of the melt is retained in the top retort.

4. Sufficient suction (8 to 10 cm.) is maintained so that the charging hole for "polysulphate" and sulphuric acid may be left open. This allows the acid charge to be added gradually.

Advantages.[1]—1. Logical working of the furnaces—good utilisation of the heat—no losses due to cooling.

2. Retorts worked at constant temperatures—long life—low upkeep.

3. Constant conditions in the condensing system—relatively small capacity for given output.

4. High HNO_3 content—low HNO_2 content in the condensed acid.

5. No vacuum pump required.

6. Simplicity of operation.

IMPORTANT POINTS IN THE MANUFACTURING PROCESS.

1. Duration of Distillation Period.

The time necessary for carrying through a distillation is dependent on many factors. If the mixture of sulphuric acid and nitrate of soda were heated in an open pot without thought of condensation, one could arrive at the minimum time required for the working of a charge. Under practical conditions the all-important recovery of nitric acid either directly condensed or obtained by absorption and oxidation of decomposition products puts a limit on the rapidity of the distillation.

Decomposition by Iron.—It is well known that iron reduces nitric acid and gives nitrogen peroxide and other reduction products, and from this point of view it would appear best to reduce the distillation time to a minimum in order to avoid excessive decomposition of the nitric acid by contact with the iron of the retort.

Retort man-lids if made of iron rapidly corrode, and even the retort lid itself shows signs of corrosion. The loss of iron from these retort parts in a measure represents the reduction effect produced on the nitric acid.

Webb[2] gives figures to show the solubility effect on the

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[1] Maugé, p. 266.

[2] *J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 219.

iron of a small scale retort, of running a nitric acid distillation. In distilling a charge of 7 lb. of nitre, the weight of iron dissolved from the experimental retort was 51·09 grams.

In the same article,[1] it is shown how the uncondensed gases from a distillation in an iron retort differ from those obtained from a distillation in glass. The following table gives the results of such distillations:—

	O_2	N_2	NO	N_2O
	Per cent.	Per cent.	Per cent.	Per cent.
Iron retort (composition of gases after 4¾ hours' distillation) . . .	1·4	92·6	5·2	1·8
Glass retort (composition of gases after 5 hours' distillation) . .	25·0	74·7	0·3	Nil

Decomposition by Heat.—It is also well known that nitric acid decomposes completely at a temperature of about 250° C. With a view to keeping this decomposition as little as possible, it is designed to work the distillation at as low a temperature as possible.

These two attempts to avoid decomposition of nitric acid in the retort are thus opposed to each other, and it is necessary to adopt some midway policy.

Decomposition of nitric acid in the retort may possibly be minimised if the temperatures in the two top flues surrounding the retort above the liquid level are kept only just sufficiently high to prevent condensation. For this purpose, with intensive working, some system of by-pass for the flue gases could be provided.

In a report (undated) on "Standardisation of Retorts, Silica Coils," at H.M. Factory, Queen's Ferry, N. V. S. Knibbs shows that the temperatures of the gases in the uptake from the retort follow closely with the temperatures of the waste gases leaving the top flue of the retort setting. Fig. 81 shows these temperatures plotted together for one distillation.

In practice it is found that very rapid distillations give more decomposition products than slow ones, other things being equal, and the conclusion is drawn that decomposition due to contact with iron is not nearly so important as decom-

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1921, 40, 218.

position due to heat. Winteler[1] draws attention to the fact that the hydrates of nitric acid boil at higher temperatures than the acid itself, and are formed with evolution of heat; so that a rise of temperature above the boiling-point of the pure acid may occur easily with decomposition of the acid and formation of these hydrates and of reduction products. As one of his conditions for efficient distillation, he says that the distillation temperature must be kept as low as possible, and to avoid overheating the distillation must be conducted slowly. Guttmann,[2] in speaking of the impurities met with in nitric acid, says that the hyponitric acid present is due to overheating in the distillation and consequent decomposition of the nitric acid. Hart[3] attributes most of the reduction of nitric acid to heat decomposition rather than to iron.

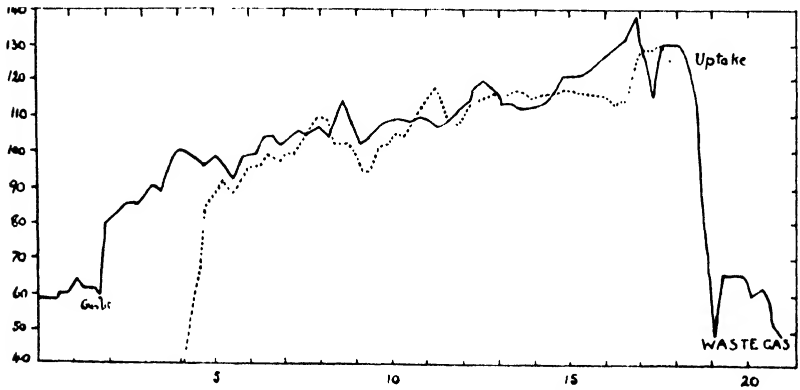

FIG. 81.—Temperatures in Retort Uptake and Waste Gas Flue.

With an absorption system of ample capacity, serious loss of the nitrogen of a charge of nitrate need not occur even with very rapid distillation, but two important disadvantages will result from the decomposition of nitric acid, viz.: (1) The ratio of strong nitric acid to weak will be reduced; and (2) the nitric acid produced will have a higher nitrous acid content than normal.

A slow distillation gives a maximum over-all yield of HNO_3; but in this case there may be disadvantages, as (1) decomposition by the iron of the pot is more pronounced and

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[1] *Chem. Zeit.*, 1905, **29**, 820-23. [2] *J. Soc. Chem. Ind.*, 1893, **12**, 203.
[3] *J. Amer. Chem. Soc.*, 1895, **17**, 580-84.

the nitric acid produced is high in nitrous; (2) fuel consumption is high.

Best all-round results are obtained when a brisk distillation is carried through without at any time allowing it to become violent.

In the author's experience, working 2-ton charges of nitrate in a 350 cub. ft. retort with Hart condenser, and a suction of 0·25 in. at the retort head in the cold, a twelve-hour distillation period proved highly satisfactory. In time of stress this period was occasionally as low as five hours, and with poor fuel and unsatisfactory labour it rose to sixteen hours.

During the early period of nitric acid manufacture at H.M. Factory, Gretna, an endeavour was made to arrive at the minimum distillation period for the condensing sets in use. For two or three days the retorts were fired very vigorously, and distillation periods as low as five hours were obtained. At the same time, however, the percentage HNO_3 content of the strong nitric acid produced fell from 92 to 90. As this acid was required to be at least 92 per cent. HNO_3, for use in the production of nitro-glycerine mixed acid, very rapid distillation practice was discontinued. With return to normal twelve-hour distillation periods the strength of the nitric acid again became normal. Although this experience does not give conclusive evidence, it tends to show that excessive destructive decomposition of nitric acid resulted from very rapid distillation. Owing to stress of circumstances this question was not further investigated at the time.

Knibbs (*vide supra*) gives figures to show that a better proportion of strong acid to weak is obtained with slow distillations, but his results in another place (Report on Experiments performed on the Queen's Ferry Gun-cotton Retorts) are not in agreement on this point. No conclusions regarding over-all recovery in relation to rapidity of distillation can be drawn from the above reports, very varying results being obtained.

As a result of plant investigation at H.M. Factory, Queen's Ferry, Fox and Robinson came to the conclusion (1) that high speed of distillation does not necessarily mean low recovery; (2) that strength of strong acid bears no relation to speed of distillation. Records of five distillations are given in their report, dated 25th December 1916, with distilling periods varying from five hours twenty-five minutes to eight hours ten minutes.

The results of Webb's experiments on the rate of distillation[1] tend to show that neither the total nitrogen recovery nor the strength of the nitric acid produced, is appreciably affected by the rate of distillation, though the evidence in the case of the small scale works plant is too restricted to admit of a general conclusion.

With distillations varying from twenty to ten hours forming part of an unfinished set of large scale plant experiments at Gretna, Poole did not find any definite relation between time of distillation and the strength of the nitric acid produced, but this work does not cover rapid distillation.

2. Drying of Nitre.

The question as to whether or not it is advisable to dry the nitrate of soda is not a very vital one in most cases. It is closely connected with the strength of sulphuric acid used and the requirements in regard to strength of nitric acid produced.

In general there is a certain weight of water introduced into the system by the sulphuric acid and the nitre, and most of this is distilled over with the nitric acid. Therefore, where nitric acid of the highest concentration is required, the sulphuric acid must be highly concentrated and the nitre dry. Distillations carried out with such materials, however, are not satisfactory as there is abnormal decomposition of the nitric acid resulting in a high nitrous content (see point No. 3).

For most purposes it may not be necessary to dry the nitre. If, however, the sulphuric acid to be used is of relatively low strength, drying the nitre may be desirable. In such a case it will be necessary to consider comparative costs of the removal of water from sulphuric acid by extra concentration or by drying the nitrate of soda.

3. Concentration of Sulphuric Acid.

This question may be looked upon from a number of standpoints according to the object in view.

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 212-20.

(a) *In Regard to Average Strength of Nitric Acid produced.*—In normal nitric acid manufacture there are two well-defined processes carried out, in one of which the average strength of all the acid produced is about 90 per cent. HNO_3 and in the other about 80 per cent. HNO_3. The latter process is carried out by distilling ordinary wet nitrate with sulphuric acid of about 78 per cent. H_2SO_4 content (Glover acid).

The former process has crystallised into the use of 90 to 94 per cent. H_2SO_4, and either wet nitre of 2 to 2·5 per cent. H_2O content or dry nitre of 0·5 to 1 per cent. H_2O content.

(b) *In Regard to Efficiency of HNO_3 Recovery.*—Naturally variation in the ratio of $H_2SO_4 : NaNO_3$ will cause variation in distillations where the same strength of sulphuric acid is used, and it would be a very big undertaking to find the best working conditions with all ratios of $H_2SO_4 : NaNO_3$.

This ratio being defined, it is possible to specify the sulphuric acid concentration for most efficient recovery of HNO_3.

With a nitre containing 1 to 2 per cent. H_2O, and using a ratio of sulphuric acid to nitre of 1·10 to 1, the following conclusions were drawn from a large number of experimental distillations carried out at H.M. Factory, Oldbury, by H. W. Webb and G. B. Stones:[1]—

1. The best concentration of sulphuric acid from the point of view of nitric acid recovery seems to be 91 to 92 per cent. H_2SO_4.
2. The amount of nitrous acid in the condensed acid decreases continuously with the reduction of the strength of the sulphuric acid used for the distillation, between the limits of 97 per cent. H_2SO_4 and 85 per cent. H_2SO_4.
3. The amount of nitrogen compounds retained in the nitre cake is greater, the greater the concentration of the sulphuric acid used, other things being equal.
4. The amount of actual nitric acid condensed increases with decrease in sulphuric acid concentration.
5. The concentration of the condensed nitric acid is greater, the greater the concentration of the sulphuric acid used.

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[1] Cf. *J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 212-20.

6. The point at which the distillation of nitric acid is very fast becomes less and less apparent as the concentration of the sulphuric acid is decreased, *i.e.*, there is much less likelihood of "blows" the lower the concentration of sulphuric acid used.

For a short period at H.M. Factory, Gretna, 98 per cent. sulphuric acid was distilled with dry nitre of about 0·5 per cent. moisture and wet nitre of about 2 per cent. moisture. The following figures represent the results obtained in working fifty 2-ton charges of nitrate:—

	Per cent. Recovery as Strong Acid 92 per cent. HNO_3.	Per cent. as Weak Acid 70 per cent.	Per cent. as Tower Acid 70 per cent.	Average Strength per cent.
Using 98 per cent. S.A. and dry nitre	77·6	10·4	11·5	85·0
Using 98 per cent. S.A. and wet nitre	76·5	11·8	12·2	84·1
Using 94 per cent. S.A. and dry nitre (for comparison) .	82·7	11·8	5·4	88·0

The working of these charges was difficult, as explosive-like evolutions of vapours were very common, and it was found practically impossible to control the distillation. Much fume escaped to atmosphere, and the work put on the absorption system was very heavy.

Sulphuric acid of such high concentration exerts a dehydrating effect on the nitric acid produced, and causes decomposition according to the equation,

$$4HNO_3 = 4NO_2 + 2H_2O + O_2.$$

General experience agrees with point No. 6 in the above report by Webb and Stones, that the distillation is quieter the lower the concentration of the sulphuric acid, other things being equal.

4. Relative Proportions of H_2SO_4 and $NaNO_3$.

This proportion was mentioned in the first page of this chapter in connection with the general suitability of retorting conditions. Generally speaking, its importance has been considered chiefly in relation to the fluidity of the nitre cake at the end of the distillation. In a continuation of the experiments on nitric acid manufacture, some conclusions of which have already been given, Webb and Stones considered this particular question.

Their conclusions are summarised below (using sulphuric acid containing 92 per cent. H_2SO_4):—

(a) *From experiments in small cast-iron still and on large scale plant.*

1. The total nitrogen recovery begins to fall off when sulphuric acid is used in such quantity as will yield nitre cake of less than 35 per cent. acidity.
2. The condensed nitric acid obtained from charges giving cakes of 38 per cent., 37 per cent., and 36 per cent. acidity is approximately of the same nitric acid content, but when a cake of 35 per cent. acidity is obtained, the nitric acid content decreases about 1 per cent.
3. The weight of nitric acid condensed gradually decreases as the sulphuric acid ratio is lessened.
4. The amount of nitrogen compounds retained in the nitre cake remains practically constant, irrespective of the amount of sulphuric acid used.
5. The amount of nitrous acid in the condensed acid appears to be a variable quantity, and apparently does not follow any variation of cake acidity.

(b) *From Experiments in Glass Apparatus.*—Conclusions 1, 2, and 3 could not be drawn from the results of the experiments in glass apparatus. Conclusions 4 and 5, however, do apply to the experiments in glass apparatus.

The tables on page 158, giving results of two large scale experiments, form part of the report by Webb and Stones.

That these results are not confirmed in ordinary large scale operations is seen by referring to summarised nitric acid production figures in the Reports on Costs and Efficiencies for H.M. Factories, controlled by the Factories Branch of the Department of Explosives Supply.

It is seen from the following table, p. 159 (Second Report on Costs and Efficiencies), that no relation is trace-

Summary of Seven Days' Experimental Run on Nitric Plant.

WEEK ENDING 15TH JUNE 1918.

Nitre Charged.	R.O.V. Used.	Condensed Acid.	HNO_3 Content.	100 per cent. HNO_3.	Absorber Acid as 100 per cent. HNO_3	Total Yield as 100 per cent. HNO_3.	Theo. Yield of 100 per cent. HNO_3	Efficiency.	Cake Acidity.	Blows	Absorber Exits.
Tons. 605	Per cent. 93·3 H_2SO_4	Tons. 431·75	Per cent. 88·3	Tons. 381·22	Tons. 32·54	Tons. 413·76	Tons. 427·34	Per cent. 96·82	Per cent. 34·4	20	Grams HNO_3 per cu. ft. 6·3
Per cent. 95·3 $NaNO_3$	...	...	...	...	..	. .	...	...	...	...	
WEEK ENDING 6TH JULY 1918.											
Tons. 688	Per cent. 93·1 H_2SO_4	Tons. 482·17	Per cent. 87·3	Tons. 420·96	Tons. 44·1	Tons. 465·06	Tons. 490·92	Per cent. 94·75	Per cent. 30·0	16	Grams HNO_3 per cu. ft. 7·3
Per cent. 96·27 $NaNO_3$	...	...	..	...	...	..	...	.	...	. .	

Efficiency of Nitric Acid Plant for quarter ending 25th March 1918 = 93·2 per cent.
" " " 29th December 1917 = 92·8 "
" " " 29th September 1917 = 93·7 "
} Cake Acidity = 30 per cent. H_2SO_4.

able on the works scale production of nitric acid between the H_2SO_4 usage and nitric acid recovery. H.M. Factory, Oldbury, with its high H_2SO_4 usage, does not get more than medium nitric acid recovery (represented by per cent. efficiency). Craigleith, with highest H_2SO_4 usage, records the lowest nitric acid recovery. Gretna, with low H_2SO_4 usage, achieves a much higher nitric acid recovery.

All the Government plants at the period under review were adequately staffed on the scientific control side, and were provided with ample nitric acid recovery systems.

January to June 1918.

Factory.	Production Tons HNO_3.	Efficiency per cent.	$NaNO_3$ Usage.	H_2SO_4 Usage.	$\frac{H_2SO_4}{NaNO_3}$
			Tons.	Tons.	
Queen's Ferry (January to May) . . .	1449·0	94·2	1·433	1·368	·955
Litherland (January to May) . . .	1909·25	90·6	1·489	1·472	·989
Oldbury . . .	8726	91·8	1·470	1·492	1·015
Craigleith . . .	1131·68	90·7	1·489	1·520	1·028
Penrhyndeudraeth . .	1100·9	90·2	1·496	1·389	·930
Queen's Ferry, T.N.T. .	14832·2	93·6	1·443	1·385	·960
Pembrey . . .	7217·8	91·4	1·477	1·379	·934
Gretna	8787·3	94·8	1·423	1·354	·952

5. Nitre Cake Acidity (expressed as H_2SO_4).

(For determination see Analysis, p. 247.)

About 98 per cent. of nitre cake consists of sodium hydrogen sulphate and sodium sulphate in the ratio of approx. seven of the former to three of the latter. Water is contained to the extent of approx. 1 per cent. Nitrogen acids are seldom present in any but very small amounts. Some sodium pyrosulphate may be present, the quantity being increased as heating is extended beyond the completion of distillation of nitric acid.

The question of acidity of the residual nitre cake is bound up with the ratio of $H_2SO_4/NaNO_3$ and the temperature at the completion of distillation.

It has already been laid down that at the completion of the distillation the residue, the nitre cake, must be sufficiently fluid to run freely from the retort. As regards consumption of sulphuric acid, it is important that the quantity of this acid should be cut down so low that a liquid nitre cake of minimum acidity should remain at the close of distillation. The fluidity of nitre cake, however, is dependent on its temperature as well as on its acidity. In general, the greater the acidity the lower is the melting-point of the nitre cake.

Since the nitric acid recovery from the distillation is closely bound up with the temperature, and since the respective values of nitric and sulphuric acid are all in favour of full recovery of nitric acid, even if it involves a slightly increased consumption of sulphuric acid, it may be generally conceded that the maximum temperature conditions determine the acidity of the nitre cake.

H. W. Webb, of H.M. Factory, Oldbury, has found it impossible to reproduce commercial nitre cake by using only sodium sulphate and sodium hydrogen sulphate as the constituents. This he puts down to the presence of other salts, *e.g.*, $Fe_2(SO_4)_3$ and $MgSO_4$, in commercial nitre cake, which may have a decided influence on the solidifying point.

Fluidity of Nitre Cake.—J. M'Leod Brown, at H.M. Factory, Gretna, as a result of observation of a large number of distillations, found that nitre cakes of acidity shown in column A would run freely from retorts when the cake temperatures were as shown in column B.

A.	B.
27 per cent.	225° C.
28 ,,	210° C.
29 ,,	205° C.
30 ,,	200° C.

He did not find any thick cakes (of acidities 28 to 32 per cent.) occur at temperatures higher than 230° C.

H. W. Webb, in the investigation referred to above, concludes that nitre cake is not a true solution but a suspension of solid in molten salt.

At H.M. Factory, Queen's Ferry, the curve given in Fig. 82 was obtained, giving the relation between acidity of nitre cakes and their solidifying points. A more useful curve would be one correlating acidity with minimum temperature at which the cake will run thin.

General experience indicates that taking all points into consideration, working to a nitre cake of. about 28 to 30 per cent. acidity gives good results. For such a nitre cake the ratio $H_2SO_4/NaNO_3$ should be approx. 0·96/1, and the final temperature of the cake should be in the region of 250° C. to 200° C.

6. Fuel Consumption.

Various factors influence the consumption of fuel, and economy in this particular can only be effected by very careful attention to the whole process of distillation. A short, brisk, continuous distillation with the "Reaction" proceeding with drawn fire will result in best fuel usage.

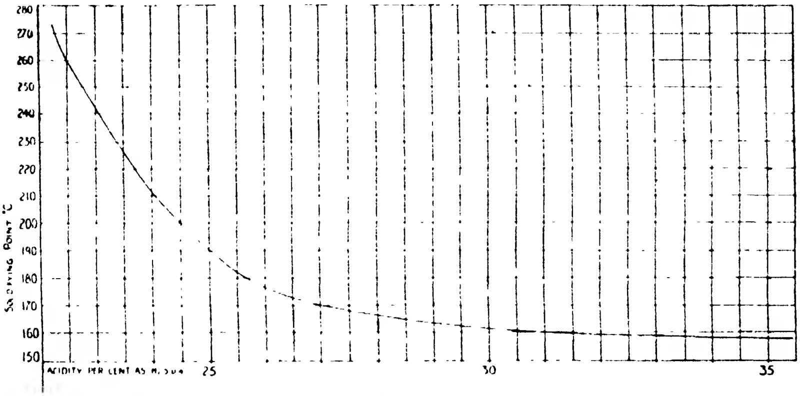

FIG. 82.—Nitre Cakes. Solidifying Point and Acidity Curve.

At H.M. Factory, Gretna, many tests were made of gas consumption during nitric acid production, and the figures obtained may be taken as representative of various types of distillation.

The gas used was producer-gas of an average composition:—

CO_2	4·0	per cent.
CO	28·0	,,
H_2	11·1	,,
CH_4	1·4	,,
N_2	55·5	,,
	100·0	

One ton of coal produced 130,000 cub. ft. of gas (N.T.P.), and an average distillation used about 30,000 cub. ft. in producing 1·43 ton HNO_3. This works out to a consumption of 0·16 ton of coal per ton of HNO_3 produced.

In twenty metred distillations the gas consumption varied from 19,871 cub. ft. to 40,928 cub. ft.

Figs. 83 and 84 show gas consumptions, recorded half-hourly, alongside flue temperatures for three different distillations. The result of low initial temperatures on fuel consumption is clearly seen when Cycle I., Fig. 83, is compared with Cycles III. and IV., Fig. 84. The distillation charted on Fig. 83 was started after a week-end shut down of the plant.

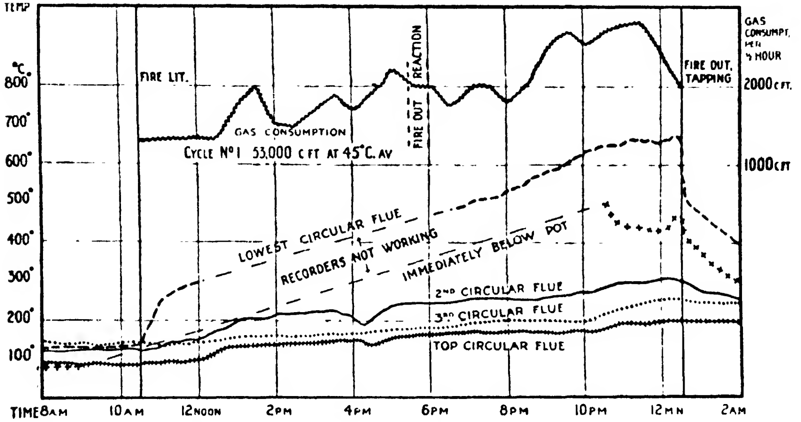

FIG. 83.—Gas Consumptions and Flue Temperatures during Distillation.

7. Decomposition of Nitric Acid.

Nitric acid is a powerful oxidising agent, readily giving up oxygen and thereby becoming reduced. The direct reduction products are HNO_2, NO_2, N_2O_3, NO, N_2O, N_2, and H_2O, chief of which are NO_2, NO and H_2O. Various factors are present during the distillation of Chili nitrate with sulphuric acid to promote the reduction of the nitric acid produced.

By Chlorine.—Chlorides are present to the extent of about 0·5 per cent. in commercial nitrate, and the action of sulphuric acid on these chlorides leads to liberation of hydrochloric acid. This hydrochloric acid becomes largely oxidised by the nitric acid produced, with consequent formation of reduction

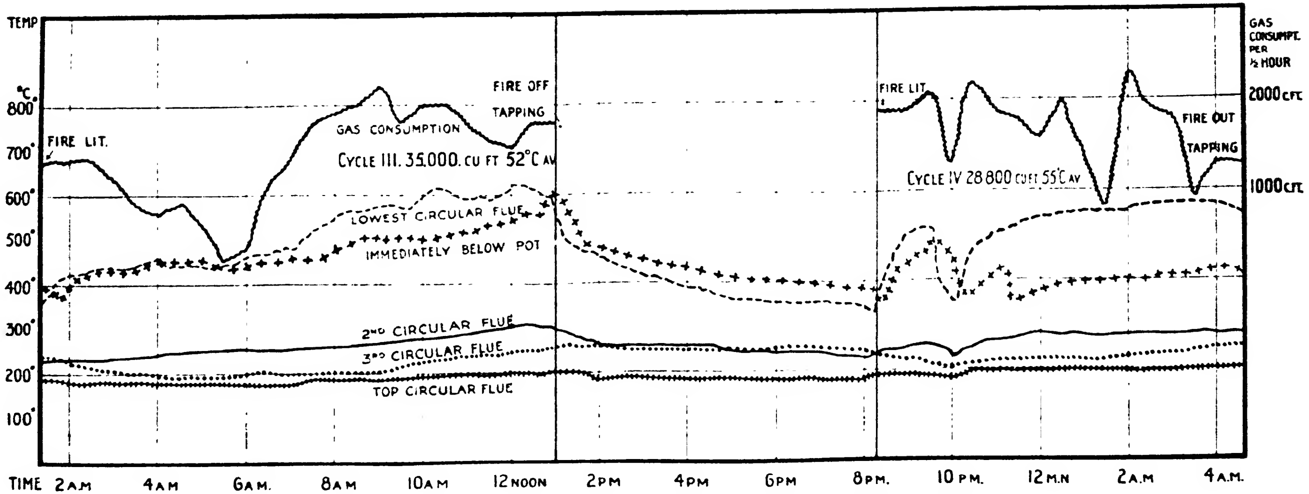

FIG. 84.—Gas Consumptions and Flue Temperatures during Distillation.

products of nitric acid and chlorine as shown in the following equations:—

$$\begin{aligned}
&(1)\ 2HCl + 2HNO_3 = 2H_2O + Cl_2 + 2NO_2\\
&(2)\ 6HCl + 2HNO_3 = 4H_2O + 3Cl_2 + 2NO\\
&(3)\ 3HCl + HNO_3 = 2H_2O + Cl_2 + NOCl
\end{aligned}$$

The gases thus formed pass forward to the absorption system, where a certain recovery of their nitrogen content is effected with re-formation of nitric acid. Traces of the hydrochloric acid are retained by the condensed nitric acid and constitute one of the common impurities of the commercial acid.

By Iron.—The retort in which the reaction is carried on is made of cast iron, which dissolves in nitric acid, producing nitrate of iron and gaseous reduction products of nitric acid. It is very noticeable that the coldest parts of the retort, viz., the small nitrate charging lid in particular and the lid in general, are most readily acted upon by the nitric acid. Owing to their relative coolness, deposition of nitric acid or its hydrates is effected at these places with comparatively rapid corrosion. Amongst the reduction products of nitric acid so produced are chiefly nitrogen peroxide and nitric oxide, with a little nitrous oxide and some nitrogen. Neither of the latter two gases is condensed or converted anywhere in the system, so they pass out of the fume stack as inevitable loss of nitrogen. The nitrogen peroxide is to some extent soluble in the condensed nitric acid, to which it imparts a reddish colour.

By Heat.—Nitric acid decomposes progressively under the influence of heat, and at 250° C. under pressure is completely converted into its decomposition products:—

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

During the progress of distillation the temperature is sufficient to cause some decomposition as here indicated with production of water, nitrogen peroxide, and oxygen.

By Carbonaceous Matter.—Carbonaceous matter, *e.g.*, straw, string, coke, etc., admitted carelessly with the retort charge, promotes decomposition of the nitric acid. Care should be taken that such materials are not allowed to get into the retort.

By Sulphuric Acid.—Highly concentrated sulphuric acid exerts a dehydrating action on the nitric acid produced, and causes the same decomposition as is represented in the above equation.

8. Blows.

A "blow" is an explosive liberation of gases from a retort by some outlet other than the normal condensing system, either the man-lid of the retort or a portion of the gas uptake being lifted by the pent-up volumes of vapours clamouring for expansion from the retort. (The roar of a powerful "blow" is something to be remembered.) The chief cause of blows is no doubt excessive firing near the "Reaction" stage of the distillation, but the view is widely held that a blow may develop or be assisted to develop by the sudden dislodging of a large bulk of hitherto unacted upon nitrate into the otherwise very active mass at the time of "Reaction."

In charging a retort the nitre may lie in a cone-shaped heap. On wetting with sulphuric acid the peak of this cone may be partially isolated from the reacting mass by a ring of soaked and hardened nitre. If the peak finally falls to pieces at the "Reaction" stage the conditions for a blow are present. To avoid this possibility, it is as well to straighten out the nitre charge with a long rake before running in the sulphuric acid.

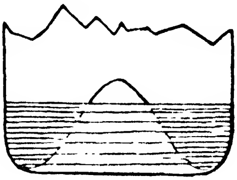

FIG. 85.

It will be readily understood that blows should be avoided, as they cause destruction of plant, entail loss of nitric acid, and endanger the health of workers.

If a blow does occur, the fire should be put out at once (if this has not already been done), and all possible steps taken to cool off the retort by opening the fireplace door, explosion doors, etc.

Workers should stand clear ready to make good the breach in the system as soon as the violence has subsided sufficiently. If the hot vapours impinge directly on to woodwork this may be set on fire, and a water supply should be available to deal with such cases.

9. Cooling of Retorts.

In normal easy working there is usually an interval of at least several hours between the completion of one distillation and the beginning of the next in the same retort. In intensive working it may be necessary to work successive distillations as rapidly as possible, and the question may arise as to when it is safe to recharge a retort which has just been emptied of nitre cake ("tapped").

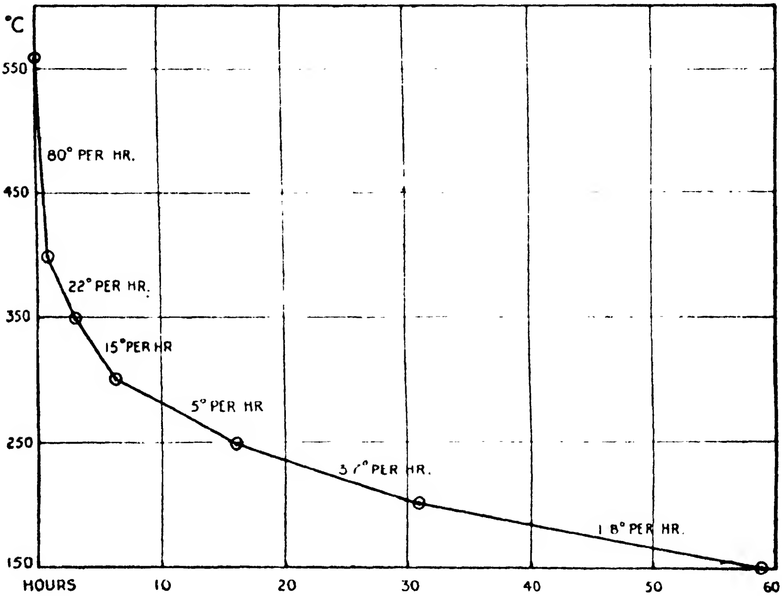

FIG. 86.—Flue Cooling Curve.

After a retort is tapped the temperature of the metal rises owing to the radiation of heat from the intensively hot and enclosed brickwork of the combustion chamber and flues (see p. 122 and Fig. 74). Only after the lapse of some time, depending on a variety of circumstances, does the retort start to cool. If, therefore, there is a desire for cooling the retort before recharging, the interval given must be sufficient to allow for the above conditions, or the "cooling" period may chance to prove just the reverse, with uncomfortable conditions of rapid distillation on charging.

In intensive working it is best to recharge immediately the retort is tapped. The introduction of the nitre and acid is then sufficient to keep the charge sufficiently cool to prevent immediate distillation. In this case it will be seen that rapid charging of sulphuric acid is advantageous.

The rate of cooling of the lowest circular flue of a retort setting is shown in the accompanying graph, Fig. 86. From this it is seen that the cooling is a very slow process in its later stages.

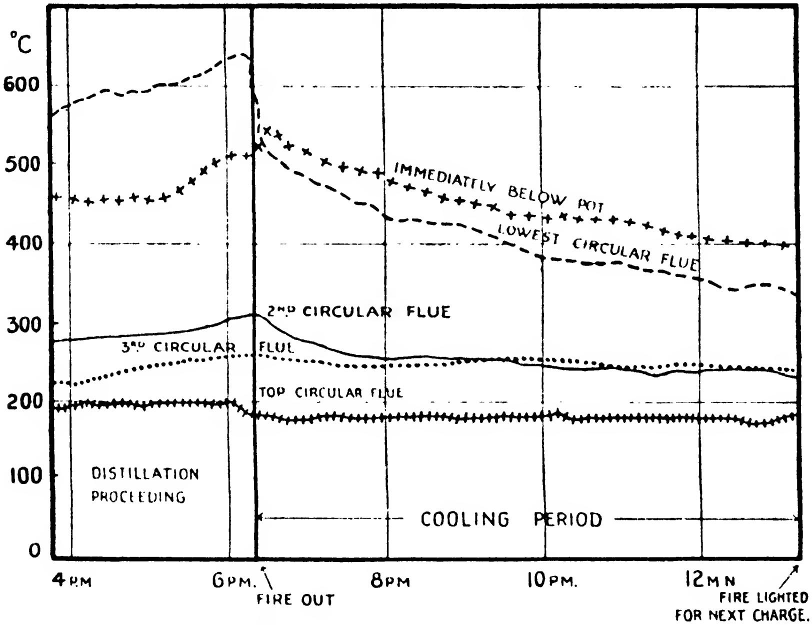

FIG. 87.—Temperatures in Flues during Cooling Period.

Fig. 87 shows temperature records of four thermo-electric pyrometers resting in the flues of a pot during a cooling-down period between two distillations.

10. Cracking of Retorts.

This subject has already been referred to on p. 51, in connection with the material for retorts.

Cracking of a retort may be due directly to corrosion, to alternate expansions and contractions with consequent failure of the metal, or to a combination of these. Rhead[1] attributes the cracking of cast-iron nitration pans to the bursting pressure produced by the increase in volume due to corrosion.

Of 31 2-ton retorts which cracked in use at H.M. Factory, Gretna, the average life was 234 charges. Of 24 retorts which did not crack, the average life was 385 charges. The retort of longest life worked 550 charges and did not crack. One retort worked only 22 charges before cracking. This was a comparatively flat-bottomed retort originally made for H.M. Factory, Henbury. The average life of 5 Henbury retorts which cracked in use at Gretna was 47 charges, while 16 Henbury retorts averaged 93 charges each without cracking. These figures tend to indicate that flat-bottomed retorts do not stand up to nitric retort-work as well as those with more rounded bottoms, but as other factors may have been at play the evidence is not conclusive.

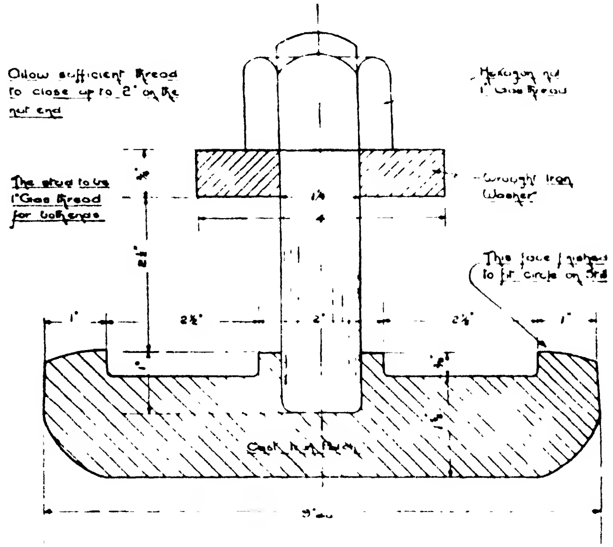

FIG. 88.—Full-sized Section of Circular Mushroom Patch, to fit on Inside of Pot Nitric Acid Stills.

Repairing Cracked Retorts.—Various devices may be

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[1] *Chem. Trade J.*, 9th February 1918, 111.

used to extend the life of a cracked retort without having to remove it from its setting. The cracks may be cleaned and filled with various compositions, welding may be resorted to, or patches may be applied internally or externally. Of these methods, patching has generally proved best. At Gretna the average extension of life of 15 retorts by patching was 82 charges, though in some cases the patches had to be refixed occasionally. The greatest extension of life by patching was 252 charges. In this case the patch was refixed twice.

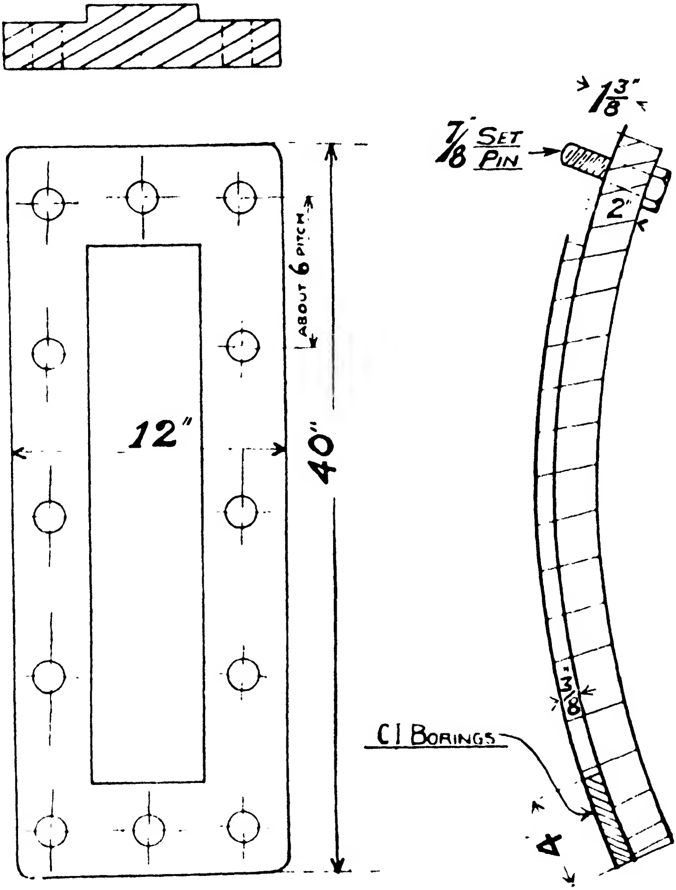

FIG. 89.—Detail of Patch for Inside Bottom of Retort.

A common way of patching is to fill in the cracks with

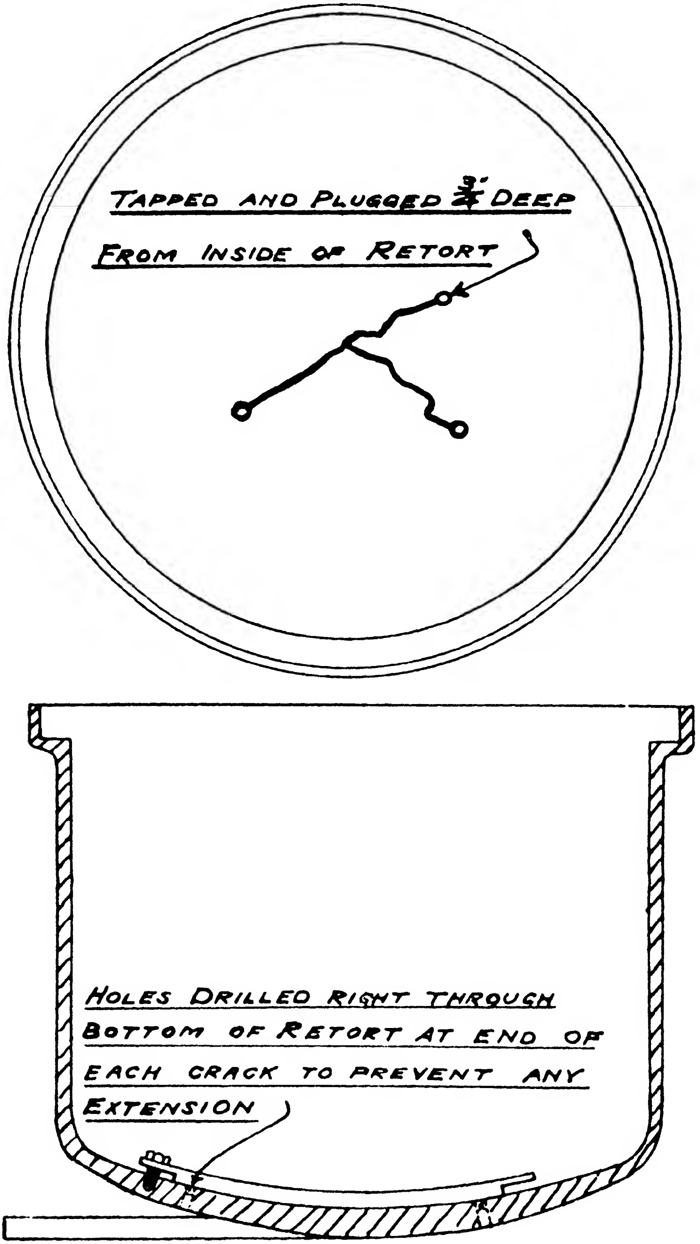

FIG. 90.—Method of preventing any Extension of Fracture.

rust jointing, p. 127, to spread a thin layer of the same mixture under the patch specially cast for the purpose, and to draw this to its bed by ¾ in. bolts.

Various methods of patching are illustrated in Figs. 88 to 90.

11. Frothing and Boiling Over.

Occasionally, and particularly when the distillation is about two-thirds through, there is a tendency for the reacting mass in the retort to froth up very considerably, even to the extent of oozing out at the man-lid, or to being carried along with the vapours to the condensation system. Frothing is more noticeable when using weak sulphuric acid. This frothing must be reckoned with by having a retort of sufficient capacity to allow it to take place without overflowing. In addition careful firing must be practised. Formerly a "catch pot" was always provided before the vapours entered the condensation system proper to act as a trap for any reacting mass forcibly ejected from the retort. This "catch pot" should not be necessary, as there should not be any boiling over.

12. Impurities in Commercial Nitric Acid.

The most common impurities are iron, nitrous acid, chlorine, and sulphates. The sources of iron, nitrous acid, and chlorine have already been indicated (p. 162). Traces of sulphate may get over into the condensing system by actual transference of retort contents (boil over), or by high final temperatures leading to some dissociation of sulphuric acid.

The nitric acid manufactured at H.M. Factory, Gretna, had only traces of impurities, as is shown by the following typical analysis:—

	Calculated as	
Sulphate	H_2SO_4	0·009 per cent.
Free chlorine and other halogen acids .	HCl	0·032 ,,
Total foreign acids	HNO_3	0·067 ,,

If condensation of the nitric acid is effected at as high a temperature as possible, the proportion of nitrous acid finally retained by the acid will be relatively small, as also the proportion of chlorine.

Crawford[1] has found minute traces of tetranitromethane,

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1922, **41**, 321-24.

monochloronitromethane, and dichlorodinitromethane in commercial nitric acid, their formation being probably due to the presence of traces of chlorides and of organic matter in the nitrate of soda.

Tetranitromethane and monochloronitromethane were found to cause very low heat tests when present in nitroglycerine.

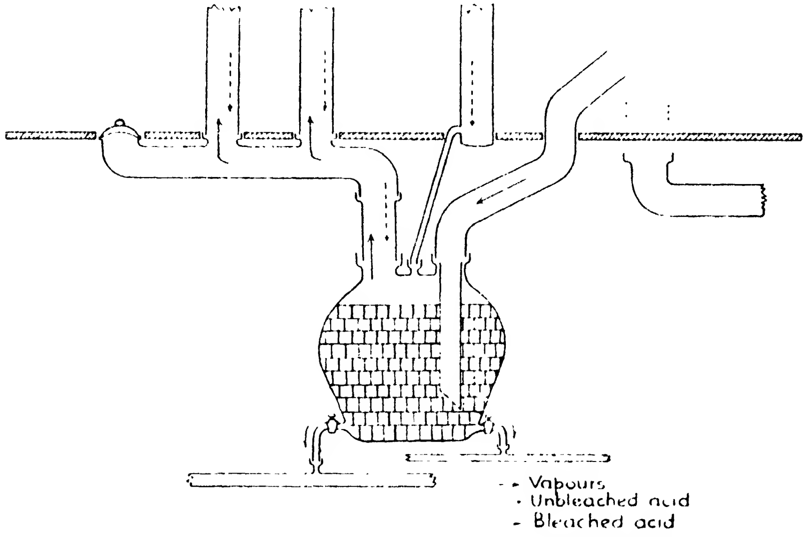

FIG. 91.—Sketch to show Method of Fitting Nitric Acid Bleacher to Stills.

13. Bleaching.

"Bleaching" is the process used for eliminating from concentrated nitric acid dissolved nitrogen peroxide and nitrogen trioxide, which impart to the acid a dark colour, with a view to obtaining a whiter acid containing a lower percentage of dissolved lower oxides.

In some condensation systems a device is made use of for bleaching the condensed acid by allowing it to flow over some packing material in a vessel receiving the hot gases direct from the retort (*cf.* Skoglund's apparatus, p. 73). By this means the nitrous acid content of the final acid need never be above 0·5 per cent. Without this bleaching device a good commercial acid of 92 per cent. HNO_3 content usually contains 0·5 to 1·0 per cent. nitrous. As an instance of this purifying action of the hot gases, note is here made of a scheme put in operation

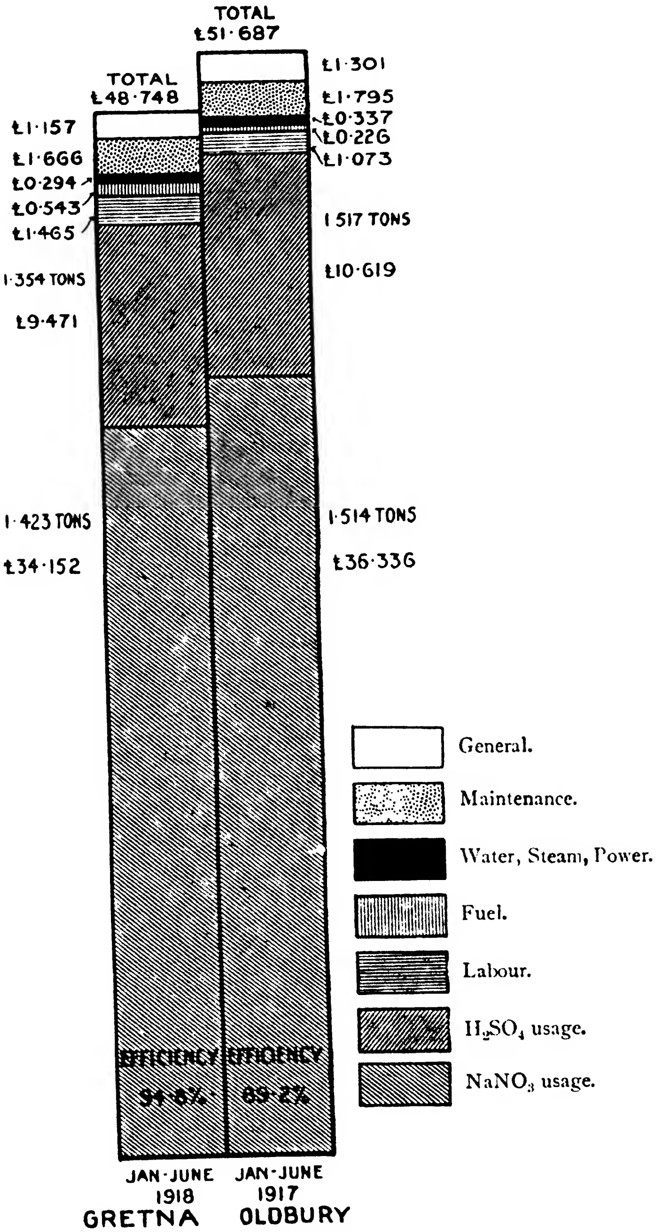

FIG. 92.—Effect of Efficiency on Cost of Production.

at H.M. Factory, Gretna, for reducing the nitrous acid content of nitric acid produced by distillation of nitro-cotton spent acid with concentrated sulphuric acid (see p. 179).

This bleaching device was a large earthenware bottle packed with acid-proof earthenware ring packing, to the bottom of which the hot vapours from the still were led, and through which they travelled from the retort to a Hart condensing set. The condensed acid flowed down the packing and was run off from the bottom of the bottle. By this means a 92 per cent. nitric acid had its HNO_2 content reduced from 2 to 2·5 per cent. to 0·5 to 0·8 per cent.

Such a "bleacher," but made of acid-resisting iron, is now an essential part of the condensing system at many works.

IMPORTANT POINTS BEARING ON COST OF PRODUCTION.

1. Efficiency of Recovery.

Usage of Raw Materials.—The main items in the cost of nitric acid are the raw materials, sulphuric acid and nitrate of soda, and it is therefore highly important that as much nitric acid as possible should be produced from the quantities of raw material used. In other words, one should aim at 100 per cent. efficiency of nitric acid recovery. The foregoing graphs (Fig. 92), from the Second Report on Costs and Efficiencies for H.M. Factories, controlled by the Factories Branch, Department of Explosives Supply, to which attention is directed for extensive information on this subject, give a clear indication of the effect of efficiency of production on the cost.

Note.—Efficiencies shown on graphs are 2 per cent. lower than the actual plant efficiencies (*vide* Second Report, p. 130, para. 2).

Efficient Control.—Economical and efficient usage of raw materials can only be brought about by careful control. It has often been shown that the most delicately adjusted apparatus and methods will not give good results in the hands of incompetent workmen. Close attention to the charges of sulphuric acid and nitre is well repaid.

The question of charging the retort is not the only one influencing efficiency of recovery. There is the question of

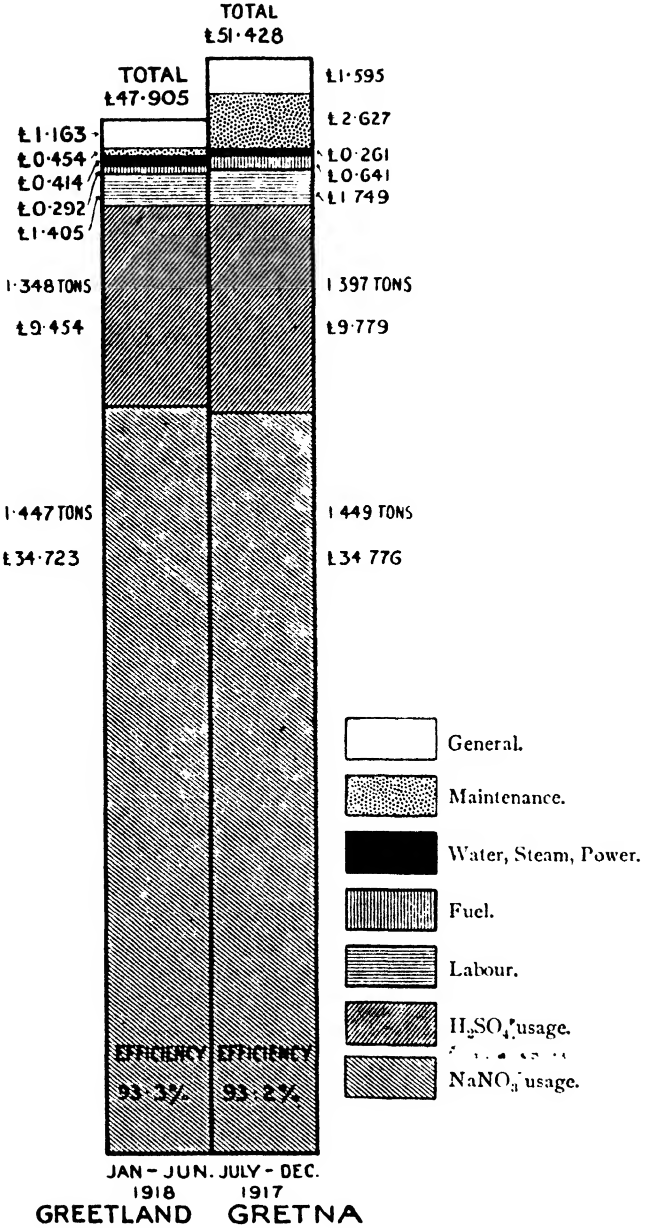

FIG. 93.—Effect of Plant Maintenance on Cost of Production.

actual recovery of available nitric acid, first in the condensing and then in the absorbing system. Bad working of the plant may result in "blows," with consequent loss of acid. Inattention to the joints in the condensing system may lead to serious loss of both gases and condensed acid. Inefficient working of the absorption system may mean serious loss of potential nitric acid. It is evident, therefore, that for maximum efficiency in recovery of nitric acid, the plant has to be run in the best possible manner, and neglect cannot be allowed to creep in at any point. Unfortunately, neglect very often does occur, and unless good control is exercised over the workers by some-one capable of understanding the true meaning of efficiency, avoidable losses will certainly occur.

2. Destructive Effects of Nitric Acid.

Maintenance of Plants.—Consideration of the comparative figures with reference to costs of production of nitric acid compiled in the Government Reports on Costs and Efficiencies already referred to, shows that maintenance of plant and buildings is one of the most important of the lesser factors influencing the cost of production.

The graphs on page 175, from the same source as those on the preceding page, show the effect of high maintenance charges in putting up the price of nitric acid.

Few commercial manufacturing processes are so destructive to plant and buildings as is the production of nitric acid. Leakage of nitric acid leads to rapid destruction of wood and iron work, to disintegration of stone, to dissolution of mortars and cements, with consequent destruction of built-up walls and floors. Leakage of nitric acid vapours results in rapid corrosion of iron work, and in a tendency to general disintegration of most building materials.

Lack of attention, therefore, to the nitric plant involves more than mere loss of efficiency. It involves the use of additional labour to do necessary repair work, and puts up the costs on account of renewals.

It is perhaps as true in nitric acid plant as anywhere that neglect breeds neglect, and once allowed to creep in, slipshod, wasteful methods of procedure are sure to become acknowledged

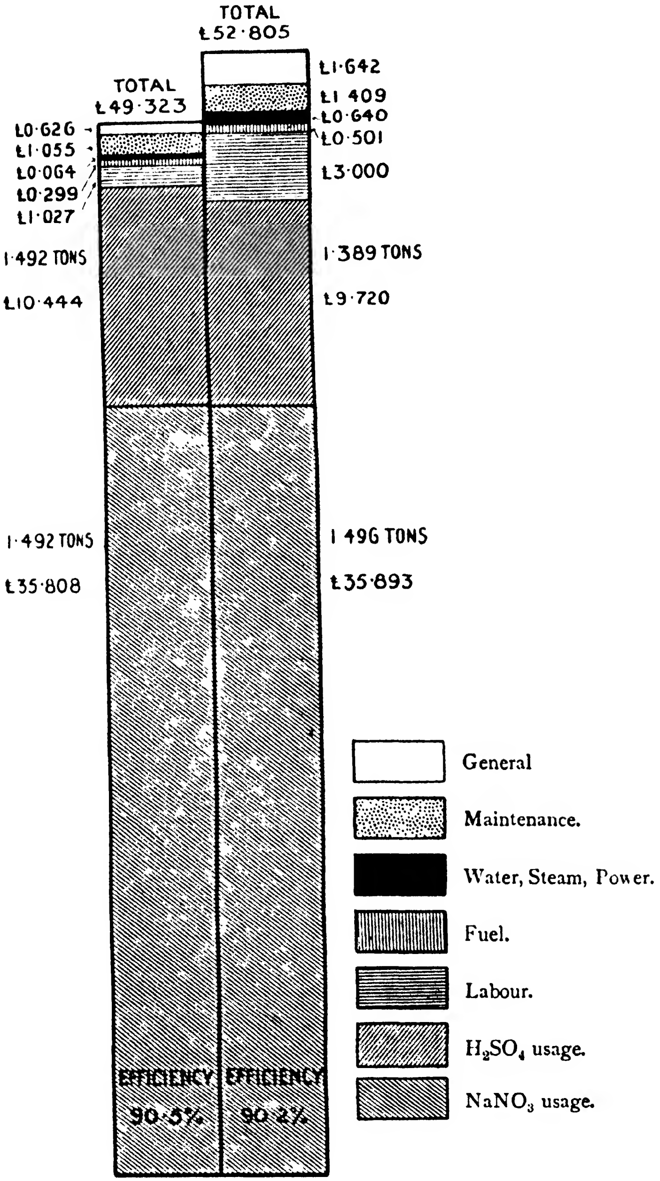

Fig. 94.—Cost Figures for Two Factories each for a Period of Six Months.

as normal practice. This may be considered the moral aspect of efficiency.

8. Labour Requirements.

The influence of the cost factor due to labour is seen by reference to Fig. 94 which shows costs for two factories, having approximately the same efficiency as regards consumption of raw materials, over a period of six months. Although other items show higher charges at the second factory, it is seen that the main factor causing the overall cost of production to be greater than at the first factory is cost of labour.

BLEACHING.

This matter has already been referred to on p. 73 in connection with the removal of lower oxides of nitrogen from nitric acid at the time of condensation. Where this method is not practised, it may often be considered desirable to reduce the nitrous acid content of the acid as obtained in the receivers. This bleaching process usually consists of blowing air, preferably heated, through the acid in vessels suitably connected to some fume recovery system. Loss of nitric acid is possible in this process.

CONCENTRATION PROCESSES.

It is often found necessary to concentrate solutions of nitric acid, particularly in explosives manufacture, where for nitration purposes only concentrated acid of approximately 92 per cent. HNO_3 content can be used. Distillation of nitric acid alone does not serve to produce acid of a strength greater than 68 per cent. HNO_3, which acid is a constant boiling mixture of nitric acid and water. Acid of lower HNO_3 content on distillation loses water until this strength is reached, and then the constant boiling mixture distils over as 68 per cent. nitric acid.

Concentration is usually effected by distilling weak nitric acid with concentrated sulphuric acid. The sulphuric acid retains the bulk of the water, becoming itself diluted, whilst the volatile nitric acid distils over, carrying with it only a small proportion of water.

This distillation is usually effected either from pot stills or in heated vertical columns, and numerous devices have been patented for this purpose.

The question of mixing sulphuric acid with weak nitric acid in preparation for distillation is considered in Chapter V., p. 282, and the actual distillation will here be considered under the two headings of Pot Distillation and Column Distillation.

Pot Distillation.

The Still.—A retort such as is used for nitric acid manufacture serves excellently as a still for the concentration of nitric acid. The run-off pipe, which ordinarily delivers nitre cake, must be fitted with a cast-iron valve and a delivery pipe for control of discharge of the weak sulphuric acid resulting from the distillation. The nitric acid vapours may be led from the still to any suitable condensing and absorbing system as already described under nitric acid manufacture.

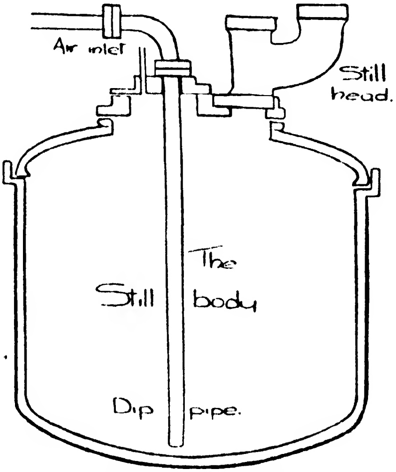

FIG. 95.—Nitric Acid Still.

A modification of the normal nitric acid retort used for recovery of concentrated nitric acid from diluted mixtures of nitric and sulphuric acid produced in nitration of cotton has no outlet pipe cast with the body of the pot. With this type of still, the residual sulphuric acid, after distillation of the nitric acid, is discharged up a cast-iron or preferably Narki type pipe permanently supported vertically within the still, and reaching to the bottom, by the introduction of compressed air over the surface of the acid. In such a case the vapour delivery pipe from the still is specially designed to allow a plug to be introduced when the application of air pressure within the still is desired.

During distillation a plug is luted in at A, Fig. 96, and the vapours travel to the uptake pipes and the condensing system.

At the close of distillation the plug is removed from A, and another inserted at B and fastened down by a clamp. The still is thus closed ready for discharge of acid up what is known as the "dip" pipe. This Narki dip pipe is bolted outside the still to a flanged lead pipe which serves for the discharge of the residual sulphuric acid to some receiving vessel. By a suitable arrangement of C.I. valves the residual acid discharge pipe may also serve for the introduction of fresh acids to the still. Such an arrangement is indicated in Fig. 97.

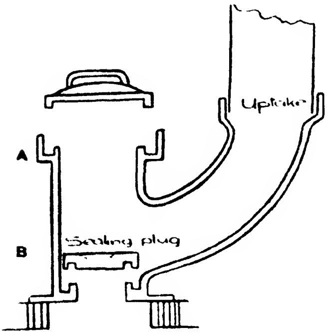

FIG. 96.—Still Head.

A small diameter iron pipe with a rubber tube connection, which may be clipped during distillation, serves for the admission of air at a pressure sufficient to lift the acid out of the still. It is very important that the minimum air pressure be used, and a mercury manometer should be installed on the air supply pipe as an indicator. Any considerable increase of pressure may lead to the lifting of the cover from the still. This cover must be jointed securely to the still by a good rust joint to ensure a closed vessel for discharge purposes.

The Distillation. — The distillation presents no difficulties, and so long as the firing is good, a rapid but steady evolution of nitric acid may be maintained. Condensing, receiving, and absorption systems may be identical with those already described under manufacture of nitric acid, and thus do not need to be outlined here.

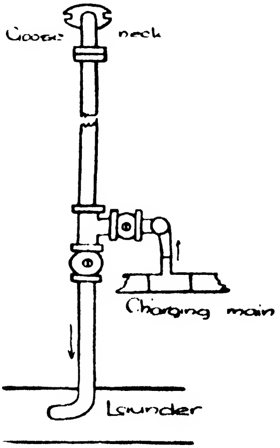

FIG. 97.—Plan of Charging and Blowing Pipes.

Vapours begin to pass over when the temperature in the first uptake pipe is 90° C. Most of the distillation is carried on with the temperature registering 135° C. The temperature is pushed to 145° C. for completion.

By this process not all the nitric acid is obtained highly concentrated, but by collecting the distillate at various stages acids varying from 100 per cent. T.N.A. downwards may be obtained, the total run of acid averaging 90 per cent. T.N.A. with only a small percentage of nitrous acid.

Residual Sulphuric Acid.—The residual sulphuric acid in the still at the completion of distillation is at a temperature in the neighbourhood of 200° C., and the transference of sulphuric acid of 78 to 80 per cent. H_2SO_4 content at this temperature is a somewhat difficult problem. Many methods have been used, but generally the plant requires a good deal of attention and repair. Lead pipes laid in water troughs become distorted and tend to choke rapidly with ferric sulphate. Open lead launders lying in troughs containing running water are more successful, but become very distorted and entail a lot of upkeep. Perhaps the best method is to receive the hot discharge in as large a volume as possible of previously discharged and cooled acid, using cooling coils if necessary. For this purpose steel tanks and cooling coils should be possible if the acid is of 75 to 80 per cent. H_2SO_4 content. Where necessary the uncooled acid might be conveyed along cast-iron or steel launders lined with acid-proof tiling.

Column Distillation.

When a mixture of sulphuric and nitric acids is allowed to flow down a cast-iron column packed with quartz and built in the flue of a fire, denitration of the mixture is readily effected. The nitric acid vapours may be taken from the top of the column to a suitable condensing system, while the denitrated sulphuric acid is run off from the bottom of the column and passed through a cooler to storage.

The upper portion of the column is best made of Narki type metal, and over the upper layer of quartz packing a Narki distributing plate is provided. From experience with this column it would appear best to distribute more mixed acid to the sides of the column than down the centre.

The accompanying drawing, Fig. 98, shows the general arrangement of a column capable of denitrating 8 to 12 tons of mixed acid in twenty-four hours.

The following table gives results obtained on denitrating nitro-cotton spent acid of the approx. composition 61 per cent. H_2SO_4, 20 per cent. HNO_3, 19 per cent. H_2O in such a column:—

Temperature in First Uptake Pipe after Cover of Column.	Nitric Acid.				Sulphuric Acid.		
	S.G.	Per cent. T.N.A.	Per cent. HNO_3.	Per cent. HNO_2.	S.G.	Per cent. H_2SO_4.	Per cent. HNO_3.
110° C.	1·526	98·8	94·85	2·95	1·702	76·2	trace
100° C.	1·530	102·1	97·8	3·09	1·700	...	trace
96° C.	1·535	101·5	98·4	2·3	...	...	trace
90° C.	1·543	101·3	97·2	3·07	1·693	...	0·07

RESCUE APPARATUS.

On works where nitric acid is made or handled, it occasionally happens that atmospheres are created which are highly poisonous. Chlorine, nitrosyl chloride, and nitrogen peroxide are liable to be met with in objectionable quantities when some mishap occurs. For such occasions it is advisable to have handy some form of rescue apparatus, so that if it is necessary for any worker to enter the poisonous atmosphere, he may do so without danger.

Various types of self-contained oxygen-supply apparatus, such as have been introduced for coal-mine rescue work, are available, and they are quite satisfactory to use. The principle of such an apparatus is that for a known period the wearer is independent of the surrounding atmosphere, oxygen being supplied from a cylinder and the carbon dioxide in the expired air being absorbed in caustic soda. Needless to say, any such apparatus must be kept carefully and inspected periodically, so that it shall be in perfect order when the call comes for its use.

Owing to the rarity of any mishap requiring the use of such an apparatus, there is always a danger of its vital necessity being disregarded, with a possibility that when an occasion arises for its use, it is found only after a hunt, and then unfortunately with its oxygen cylinder empty.

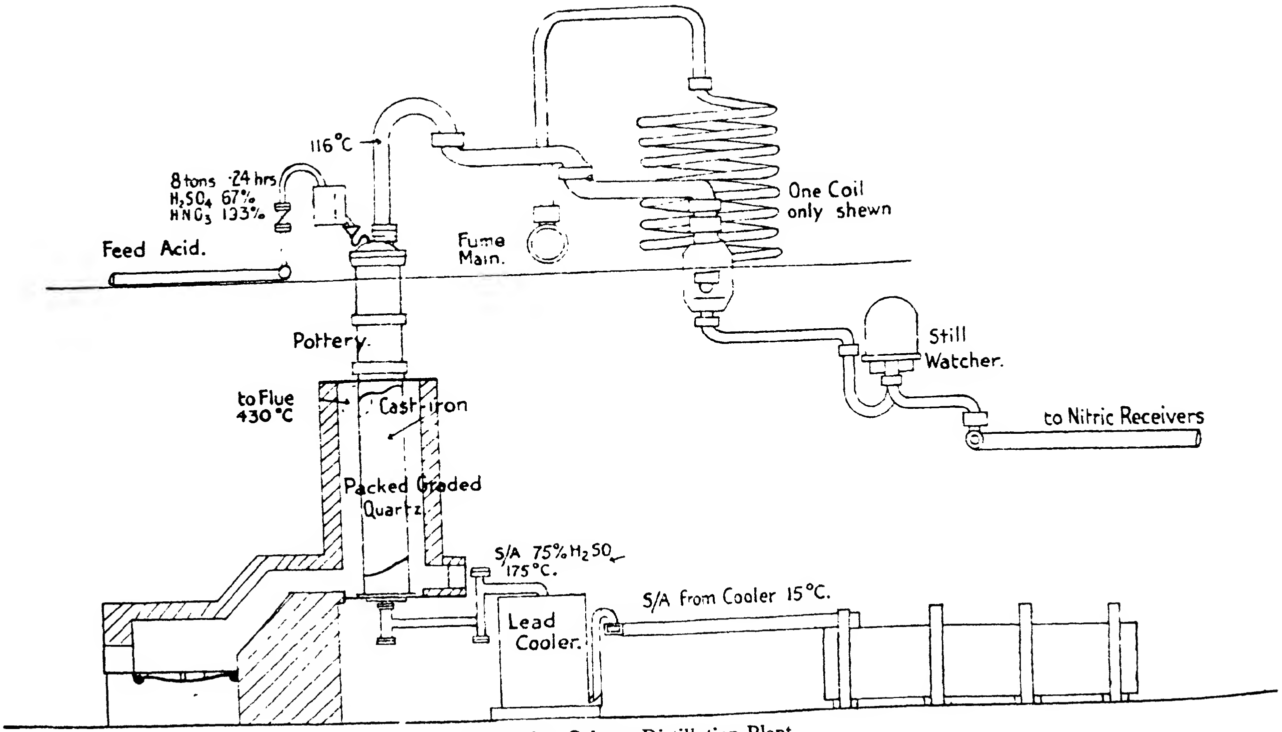

FIG. 98.—Column Distillation Plant.

Three types of oxygen-supply apparatus used by the author are:—

The Huskisson—half-hour; self-rescue.
The Salvus—half-hour.
The Meco, with helmet—two hours.

It is a good plan to provide a special locked cupboard, with key under glass, where the rescue apparatus can be kept, and along with it such auxiliaries as the following:—

Rope, Pyrene fire extinguisher, Rubber gloves, Goggles, Electric hand lamp.

It is important that at least a nucleus of the workers on acid areas should receive careful instruction in the handling of such self-contained rescue apparatus.

RESPIRATORS.

As a result of the use of poisonous gases for fighting purposes during the recent war, there are now available handy respirators of the army type for industrial purposes.

A respirator consists essentially of two parts: a face-piece and an absorption apparatus. The face-piece may consist only of a mouth-piece and nose-clip, but this form causes much discomfort and affords no protection to the eyes. The second and more recent form is a complete mask of rubber fabric with eye-pieces of "Triplex" glass so arranged that the incoming air passes over the inner surface of the glass, thus preventing dimming by moisture from the breath. This form requires neither the use of a mouth-piece nor of a nose-clip, and may be worn for a much longer period than the former type. The purifying canister is of the form used in the small military box-form respirators, and the substances employed for absorption should have a high capacity and rate of reactivity for the gases to be removed from the inspired air. The absorbent found useful for acid gases consists of granules of slaked lime, kieselguhr, and ferric hydroxide along with absorbent charcoal. Where smoke and acid mists are to be encountered, it is advisable also to include a pad of fine felt as a filter.[1]

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[1] L. Levy and G. W. West, *J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 235.

Fieldner, Teague, and Yoe[1] state that army gas-masks should never be used in atmospheres containing less than 12 per cent. oxygen by volume. The non-oxygen-supply type of respirator may be successfully used in atmospheres of relatively low poisonous gas concentration for short periods, and has the great merits of handiness and simplicity. It should not be regarded, however, as universally safe, and in cases of doubt the oxygen-supply type of apparatus should be used.

As a protection against the irritating effect of acid mist, and for very short spells of use, pads of cotton wool and gauze, previously damped, may be used to cover the mouth and nostrils.

ACID BURNS, POISONING BY ACID GASES, MEDICAL EQUIPMENT.

Dr G. A. Welsh, medical officer for the Dornock area of H.M. Factory, Gretna, during the war, has kindly placed at the author's disposal a complete report of his experiences in the treatment of acid burns and gassing arising directly from acid manufacturing plants and from nitro-cotton and nitro-glycerine nitration plants. The report covers 4028 slight, 226 severe, and 38 serious acid burns, and 361 cases of gassing, from which it is seen that Dr Welsh's experience in the treatment of such cases has been very extensive.

The use of raw untrained labour, largely of poor quality, resulted in the number of accidents being greater than would be considered normal.

Apart from a detailed list of individual cases, Dr Welsh's report is given in substance below.

In the case of a small factory or plant where it is not feasible to retain the services of a medical officer, there is no reason why an external medical authority should not be called in to advise as to first-aid equipment. At least one of the employees should have had a recognised training in first-aid work, and he should be made responsible for the superintendence of all first-aid equipment. A small room in the administrative offices, provided with a hand basin, camp bed, and simple medicine chest, should be set aside as a dressing station, and this room should be kept scrupulously clean.

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[1] *J. Ind. Eng. Chem.*, 1919, **11**, 622-23.

Acid Burns—by Dr G. A. Welsh.

General Considerations.—In dealing with the subject of acid burns in a factory such as H.M. Factory, Gretna, where the production of acid is on a large scale and constitutes an engineering as well as a chemical problem, I propose to do so by introducing short descriptions of things not purely surgical which will elucidate the points I want to emphasise. For the purpose of descriptions I have divided those working the plant into (*a*) operatives whose work is chiefly chemical, and (*b*) operatives whose work is chiefly mechanical, though in practice it is difficult, I admit, to maintain such a hard and fast distinction. In the case of (*a*) it is possible to protect the exposed surfaces, *e.g.*, the hands by rubber gloves, the eyes by goggles; in the case of (*b*) it is not so possible, as the workman is using tools and cannot work so efficiently if his touch is dulled or his sight in any way blurred. This was the attitude of the workmen and made it very difficult to adopt precautionary measures. This fact is important because in the majority of cases the escape of acid from a closed system is due to an accident closely connected with a breakdown in the machinery. It is also germane to mention that the escape of acid was often sudden and with considerable force behind it due to the pressure in the system.

The mechanical operative in the ordinary course of employment soils his hands, and when the accident happens the acid comes in contact with the dirty surface, in many instances with abrasions and cuts. It did not take me many visits of inspection so see how dirty some of the hands of the workmen were, and to appreciate how difficult it would be to prevent sepsis. The importance of this point was speedily impressed upon me, as in the early days I saw numerous cases where the acid burn was so slight it gave the workman no concern at the time. He only reported for treatment when sepsis developed, and this caused an unnecessary prolongation of the period of incapacity. To remedy this I recommended the Section Manager to issue instructions for every case of acid burn to report at the dressing station. The nurse had instructions to clean the burned part and surroundings thoroughly before applying the final dressing. It took some time for this advice to be appreciated at its proper value; but eventually there was a general conversion, and many hours of labour were saved to the factory, and there was a smaller Compensation list. Arising out of this description I wish to emphasise three points: (1) that it is of prime importance to protect as far as possible exposed surfaces, *e.g.*, the hands and the eyes; (2) that it is essential to take every step to avoid sepsis; (3) that the operatives should be taught to look after the state of their hands, and pay special attention to cuts and abrasions.

Varieties of Acid.—The acids manufactured are concentrated sulphuric acid, oleum, and concentrated nitric acid. Further, these acids are mixed in varying proportions to produce mixed acids for nitrating purposes. In addition to these, the spent acids left after nitrating are denitrated and weak sulphuric acid and nitric acid recovered for further use. During the course of this denitration process, the temperature of the acid is raised to a considerable degree: in the case of weak sulphuric acid a temperature of 200° C. is reached. Lastly, there is a by-product got from the manufacture of nitric acid, an acid sulphate of soda called nitre cake, which is discharged from the retorts in a molten state at about 150° C. to cooling pans. It follows that an operative may be burned with oleum alone, with sulphuric acid alone, with nitric acid alone, with mixed acid, or with nitre cake at a high temperature.

External Appearances.—It is possible to recognise by external appearances the action of these different acids on the skin. Oleum and sulphuric acid produces a greyish-brown colour, nitric acid produces a bright yellow discoloration, mixed acid produces a reddish-brown colour with a faint yellow in it, the yellow being most distinguishable at the margin of the burn. There is in the early stages little congestion of the surface when there is no heat acting with the acid. When a burn is inflicted with an acid at a high temperature, or with the molten nitre cake, there is well-marked congestion, and bullæ are quickly formed. This congestion masks the colours produced by the same acid in the cold state. For purposes of treatment it makes no difference what cold acid produces the burn, and there is only a difference in technique, not in principle when the part is scalded as well as burned by acid. Concentrated sulphuric acid or concentrated nitric acid falling on the skin of the hands and speedily treated will produce very little effect, a weaker acid with heat produces a burn which gives more trouble. Burns of a mucous surface, *e.g.*, the lips and inside of the mouth, and a burn of the eye cause a marked reaction and take longer to heal.

First-Aid.—In dealing with acid burns everything depends upon the promptness and thoroughness of the first steps taken to treat them. We have here a first-rate example of the importance of what is known as first-aid.

First-aid boxes containing the necessary articles for treatment, and buckets of clean water, were placed all over the plant within easy reach of every operative. These appliances were regularly inspected and maintained. In addition to this, as I mentioned earlier, every case was reported to the nurse, who inspected simple cases and reported all severe cases to the doctor. All severe cases had the final dressing applied by the doctor. Cases where a mucous surface was affected, or the eye burned, were personally treated by the doctor. These boxes contained the following materials:—1 lb. white wool, 1 lb. picric wool, 1 lb. white lint, 1 lb. boric lint, 1 Winchester quart saturated solution of sodium carbonate, 1 bottle (16 oz.) Carron oil, 1 bottle (4 oz.) iodine solution and brush, 4 oz. picric gauze, 4 oz. cyanide gauze, 4 oz. white absorbent gauze, 1 doz. each 3″, 2″, 1″ O.W. bandages, 1 doz. each 3″, 2″ Dommette bandages, 1 reel adhesive plaster, 1 bottle (4 oz.) sterile castor oil, 1 bottle (16 oz.) boric lotion 5 per cent., 1 eye-bath, 1 glass eye-rod, 6 triangular bandages, 6 unit doses chloroform solution (Spt. Chlorof. m. 20, Liq. Strych. m 3, Aq. ʒ iv.), 1 doz. seidlitz powders.

Note.—Adjacent to the first-aid box was another box containing a cylinder of oxygen provided with key, reducing valve and indiarubber tube connection with vulcanite mouthpiece.

Treatment.—To ensure promptness of treatment, a brief description of what is to be done was printed and circulated to the section managers and those in authority acting under them. Eventually these rules were incorporated in the Factory Rule Book so that each operative might have the information.

Plant Instructions.—Get rid of surface acid by the application of clean water to the part; this may be done by immersing the part in a tub of water, by playing a hose on it, or by laving water on it if it is the face or head.

Neutralise the acid in the part by applying the alkaline solution and allowing it to act for ten minutes.

Gently dry with cotton wool and apply moist picric acid gauze.

Cover the surface with a layer of cotton wool and keep in position with a bandage lightly applied.

The person who is burned should not be allowed to move the affected part. If the arm is burned a sling should be applied; if the legs are burned a stretcher should be used.

He should be seen by the doctor as soon as possible.

When the part affected is the eye or the mouth, it should be washed with alkaline solution and oil applied over the surface.

Eye Treatment.—1. Immediately wash the eye well with the saturated solution of sodium carbonate.

N.B.—An eye-bath is placed in the first-aid box.

2. Drop one or two drops of the sterile castor oil in the eye.
3. Cover with a pad and bandage.
4. Report the case at once so that a doctor may see it as soon as possible.

The dressing station was centrally situated, well heated, equipped with sterilising apparatus, and had ample bath accommodation and four beds for the detention of any serious cases.

No patient was brought to the dressing station until all surface acid had been got rid of by ample treatment with cold water. In the case of plant adjoining the station, the further stages were carried out at the dressing station. In the case of outlying plant, the dressing had been applied and was removed for inspection on arrival.

On arrival the nurse obtained the history of the case, and if a simple case, dressed it and reported afterwards. In severe cases the nurse reported by telephone and proceeded to prepare the patient for examination, being particularly careful to remove all acid-soaked clothing before cleaning up the affected area and surroundings.

Before dealing further locally with a severe case, *e.g.*, one in which an extensive surface or a special area such as the head, face, neck, or eye was badly affected, I always took precautionary measures to combat shock. The patient was treated in a temperature between 65° and 70° F.; he was given a hot drink, milk or bovril, and a 60th of a grain of strychnine hypodermically. The cleaning and soaking of the burned area with alkaline solution having been thoroughly attended to, moist picric acid gauze, strength 1 per cent., was applied, and the part covered with sterilised cotton wool and lightly bandaged. The alkaline solution which I used was a saturated solution recrystallised sodium carbonate. This I found to be a very useful agent for cleaning the part as well as neutralising any free acid in the tissue. During the acute stage of the burn the dressing was changed twice daily, moist picric acid gauze being reapplied over the area. This was continued until healing was well advanced; this dressing was then changed for sterile plain gauze wrung out of normal saline solution. If the covering of the surface with epidermis was in any way delayed, I applied sterile gauze soaked in a solution of hydrogen peroxide (10 volumes). In cases where sepsis developed, I substituted for the picric acid gauze, gauze soaked in hydrogen peroxide, the pus being gently swabbed away from the surface with normal saline solution. When blisters were present over the burned area, I left them untouched for twenty-four hours; they were then pricked, being careful to make a small opening, and as much of the fluid as could be removed dried off. On or about the third day the superficial layer was excised by means of scissors and the picric acid dressing continued.

Eye Cases.—In the case of a moderately severe burn, these consist in the œdema of the conjunctiva, with well-marked injection of the burned part and its surroundings, severe pain is complained of, and photophobia is marked. If a concentrated acid gained entrance to the eye in any quantity, there is very quickly developed stasis in the corneal lymphatic system, and the cornea becomes quite milky even to the extent of the obliteration of the pupil.

TREATMENT.—As soon as possible after the burn was received the whole of the conjunctival sac was douched with the saturated solution of sodium carbonate. In the majority of cases this was done on the plant. The further treatment consisted in instilling 3 or 4 drops of 1 per cent. solution of atropine sulphate, and when the pupil became dilated a few drops of sterile castor oil. The eye was then covered with a pad soaked in boracic solution and a bandage applied. Further treatment consisted in washing out the eye night and morning with boric solution, and once in twenty-four hours instilling a few drops of sterile castor oil into the sac.

Explanation.—Before leaving the treatment of acid burns, it may be useful if I shortly summarise the points I consider important, and at the same time explain the general principles on which the treatment is based.

An acid progressively destroys the tissue so long as it is potent, and only ceases to act when its corrosive property is destroyed; the more quickly you get rid of surface acid and the more thoroughly you render the acid in the tissue inert by neutralising it, the more you limit the ultimate damage done. The cicatrix left after healing is in direct proportion to the amount of tissue destroyed, and I need scarcely add that in the case of the face and eyelids this is a matter of great importance. The thorough cleaning of the burned area and its surroundings are steps taken to prevent sepsis, with its attendant danger of absorption and system poisoning, the production of weak tissue in healing, and the formation of a dense and more unsightly cicatrix.

In the dressing of the wound the substance used should be antiseptic and as little irritating as possible; it should not be oily in character except in the case of the conjunctival sac or a mucous surface, nor should any greasy substance be applied to the skin surface. Pain is better dealt with by local application if possible, and the use of narcotics should be restricted to very severe cases. Picric acid is an ideal substance; its action in precipitating and combining with the albumin of the tissue forms a covering which is antiseptic and protective and at the same time allays pain. It has a property like that of carbolic acid in finding its way into the deeper tissue and acting there. I prefer to use it as a gauze and not as a solution painted on the surface. Its action is really on the same principle as the French substance ambrine, in sealing up the surface of the damaged area with an antiseptic layer. In the case of ambrine it is essential to dry the surface, otherwise the high temperature at which it is applied in the presence of moisture will scald the tissue. At this stage in the treatment of acid burns where the tissue has been soaked with an alkaline solution to neutralise the acid, it is not possible, nor is it desirable, to attempt to dry the surface, and for this reason I think a better result is got from picric acid, which can be applied at a safe temperature. The final results of the picric acid treatment are very satisfactory, and it is rare to have to graft skin. I have not seen any cases where cheloid developed in the cicatrix. In several of the cases where eyelids were affected, a plastic operation to relieve conditions like ectropion was necessary. In the treatment of eye cases I find that atropine relieves pain quite as much as cocaine, and has this advantage that its dilatation of the pupil is more lasting.

Effects of the Inhalation of Poisonous Gases.

The gassing conditions dealt with are chiefly those met with in nitric acid practice, reference being made to nitric acid vapour (mist), chlorine, nitrosyl chloride, nitrogen peroxide and carbon monoxide—from producer-gas.

General Considerations.—The effects of a gas or an acid mist vary according to the quantity inhaled. If a sufficient quantity is inhaled at one time the condition is properly called gassing. The signs and symptoms are acute, and except in the case of CO, are for the most part due to the irritant action of the gas. There is another aspect, however, which must not be lost sight of: if this same gas or mist is inhaled in small quantities over a long period, it is capable of causing ill-health. I propose to deal with these cases separately; they are cases of system poisoning, and not gassing. I will also deal separately with carbon monoxide, which is not an irritant gas like the others. There are, of course, differences in the effects produced. Some workers stand larger quantities than others, a high degree of resistance being developed in those thoroughly acclimatised to the work. A new hand is more readily affected than one who has been a year on the plant, and a foreman of long experience may be little affected by quantities which knock out the other less acclimatised workmen. Striking examples of this are found on plants where the gases are highly irritant and where, owing to the nature of the operations, they are more frequently found in the atmosphere — nitric acid retorts, acid-mixing, and nitric acid stills. In this connection it is of great importance that every worker should be medically examined and classified for work. A man with weak eyes, or who suffers from pharyngitis, laryngeal catarrh, or any lung affection, is not a suitable person for work on an acid plant. I have records of cases where the inhalation of a moderate amount caused a severe attack of bronchitis in a person predisposed to it, and of others where it directly caused a quiescent lung tuberculosis to become active.

Effects of Various Gases.—Volume for volume the compounds of sulphur and oxygen are not as dangerous as the compounds of nitrogen and oxygen or the compound NOCl. In a similar manner I may state that the vapours of sulphuric acid are not as harmful as those of nitric acid. A gas which is an anhydride, *e.g.*, SO_2 or NO_2, does not affect the skin; it causes smarting of the eyes and lachrymation, and acts on the mucous membranes of the mouth, naso-pharynx, larynx, and bronchi. A gaseous vapour, *e.g.*, sulphuric acid mist or nitric acid mist, in addition to affecting mucous membranes, tells of its presence by irritating the thin epidermis on the face and back of the hands.

Gassing.—A person who is gassed by an irritant gas complains first that he has difficulty in inspiration. His inspiration is shallow and frequent, and he coughs at once if he attempts to breathe deeply. With this there is breathlessness on any exertion and thumping of the heart on the chest wall. He says that his chest feels tight, and there is also a feeling of constriction in the larynx. Soon he complains of dryness and burning in the pharynx, and there is evidence of laryngeal irritation in the form of a short persistent cough. He develops a headache with throbbing over the temples, feels sick, and in some cases actually vomits. He has an anxious expression, feels ill, and has a full bounding pulse; cyanosis may show in the face and thumb nails. In the course of an hour or two there is a slight rise of temperature. Physical examination of the chest shows harsh vesicular breathing and occasionally there are some low-pitched ronchi, the heart rate is frequent, and the sounds are accentuated. If it is a severe case the extraordinary muscles of respiration are called into play. The severity of these symptoms varies with the amount inhaled.

In order to estimate the gravity of a case it is essential to know what is the substance causing gassing. With this knowledge, and judging from the severity of the signs and symptoms, it is possible to give a fairly accurate prognosis in all cases except those of NO_2 and nitric acid mist. In the case of NO_2 and nitric acid mist one must be very guarded, because the effects may be slight at the time, and give no indication of the amount of damage done to the lung. Such a case may become suddenly ill some hours afterwards, and develop acute capillary bronchitis of a suffocative variety with œdema of the lung. Cases where Cl or NOCl is the cause may appear very alarming at the time; but one knows from experience that the chances are in favour of the signs and symptoms settling down, and recovery taking place. The urgency of the symptoms in these cases is due to spasm more than tissue change. Expectoration of blood is a common occurrence in gassing; if it is small in amount and mixed with mucus, it is not of serious import; it may persist for two or three days. A large hæmoptysis is evidence of pre-existing lung mischief. In NO_2 cases expectoration of a blood-tinged serous fluid is a grave sign, indicating capillary bronchitis with œdema of the lung. Severe cases of gassing were kept under observation in the rest-room until all dangerous symptoms subsided. In the majority of cases the urgent symptoms subsided in twenty-four hours, a few lasted for forty-eight hours; it was then a question of dealing with what was left, pharyngitis, laryngitis, bronchial irritation, or bronchitis. For a few days the patient complained of being out of sorts, restless, without appetite, constipated, and sleepless.

A moderately severe case of gassing, which resolved without complications, was able to return to work in from seven to ten days. Any complication, *e.g.*, laryngitis or bronchitis, of necessity prolonged the incapacity and rendered it unwise to return the operative to work until it was fully cleared up. I always gave such cases a change of air and surroundings for a week before certifying them fit to return to work.

Gassing with carbon monoxide presents a different picture, as CO is not an irritant gas. It acts, as is well known, by combining with hæmoglobin to form CO-hæmoglobin, causing a deficient supply of oxygen to the tissue. Its affinity for hæmoglobin is greater than that of oxygen, and if present in the air breathed, its gradual absorption displaces oxy-hæmoglobin.

In all cases of CO poisoning which occurred, with the exception of two, the men inhaled the gas in small quantity, and were not seriously affected. They were working alongside other workmen, and their condition was recognised in the early stages. The two serious cases inhaled the gas in a close space; they were working alone and were found unconscious, one suffering from epileptic convulsions, and the other from heart failure. The case of heart failure was that of a chemist who walked out of his office, which contained CO, into the cold air. Both cases recovered.

Treatment of Gassing.—

PREVENTIVE.—It is very important to thoroughly acquaint the operatives of the dangers they run by inhaling poisonous gases. This was systematically done, and warning notices, especially in connection with nitrogen peroxide, were posted on the plant and incorporated in the workmen's book of Factory Rules.

The wearing of respirators by operatives was carefully considered, but after many trials it was discontinued. The operatives themselves did not like wearing them, and as the examples of gassing were generally the outcome of some accident, it was impossible to be sure that the operative would be wearing a respirator at the time. As an exception there is one case I would like to mention, that of the nitro-cotton dippers. They wore a simple respirator of moist cotton wool well over the mouth and nose. This trapped the vapours from the mixed acid up to a certain point, and they felt the benefit of it, but it could not be called efficient. Short of a self-contained apparatus nothing was found to trap NO_2

fumes efficiently. It sometimes happened that a building might rapidly fill with fumes as the result of an accident, and for this emergency we had a self-contained apparatus, the Meco, which was used (see page 182).

FIRST-AID TREATMENT.—The following instructions were printed in the Factory Rule Book:—

Nitrous Fumes.—To treat a person gassed with brown nitrous fumes—remove at once to the fresh air and lay out flat. If a severe case, he should be carried out and not allowed to walk.

Take care the heat of the body is kept up by covering with blankets, and if need be, use hot-water bottles.

One dose of chloroform solution should be given at once and the patient seen by a doctor as soon as possible.

N.B.—If there is marked difficulty in breathing, or if the face is dusky blue in colour, oxygen should be administered at once.

Carbon Monoxide.—All workers are warned that carbon monoxide is one of the constituents of producer-gas. When this gas is inhaled in a closed space it may cause serious illness to the worker.

A considerable quantity may be inhaled before its effects are produced, and the worker may become unconscious without feeling much the matter beforehand.

Giddiness, shortness of breath on slight exertion, thumping of the heart, and an unsteadiness in the legs are the symptoms which may first show themselves.

To treat a person gassed with carbon monoxide, he should be at once removed from the poisonous atmosphere, but not brought suddenly in contact with cold air, as this may produce a serious condition from heart failure. The person should not be allowed to walk, but should be carried out into a pure atmosphere and kept warm with blankets and hot bottles. If the breathing is shallow or has stopped, artificial respiration should be at once begun, and oxygen administered from a cylinder. The doctor should be informed at once of such an occurrence, and unless the person is too seriously ill to be removed, he should be taken to the first-aid station without any delay.

In slight cases a dose of chloroform mixture, followed by a seidlitz powder and a few hours' rest, was quite sufficient. If the case was more severe it was taken to the dressing station, and the patient was put to bed and plenty of fresh air allowed to play round about him; his bodily heat was maintained by means of blankets and hot bottles until a state of mild perspiration was reached. Marked difficulty in breathing and cyanosis were treated by administering oxygen. A dose of chloroform mixture was administered every four hours, and in the way of food nothing but hot milk was given.

In the case of NO_2 poisoning, the administration of oxygen was continued until all signs of danger were passed.

Death from Nitrogen Peroxide Poisoning.—Only one case of gassing had a fatal termination. This was a man who was working in a closed space, inhaled the vapours of fuming nitric acid, and died from the effects of nitrogen peroxide.

Cases of System Poisoning.—From time to time examples of what are called system poisoning came before my notice. This happened in operatives who had never suffered from gassing, but who from time to time had inhaled small quantities of fumes. I have no doubt, after careful inquiry, that it was the inhalation which caused the condition. A common history was that the onset was gradual, that the condition became worse after each successive inhalation, and that eventually the patient became unfit for work. Such a case was anæmic, complained of headache, sleeplessness, loss of appetite, loss of energy and capacity to do work. The case suffered from a torpid dyspepsia, with marked flatulence and constipation. In treating these cases I found that as long as they were kept at work no system of treatment benefited their condition. As soon as they were removed from work and sent for a change of air, very simple treatment put them right. The most successful method of treatment for these cases was to put them on a light fluid diet and treat them with an alkaline saline mixture.

A number of cases from inhalation of small quantities suffered from acute gastro-enteritis. I also saw operatives with numerous ulcers affecting the lips, buccal mucous membrane, and pharynx. These ulcers were intractable and resisted all forms of treatment as long as the patient remained at work;

when he was removed from work a simple mouth-wash sufficed for their healing. A number of cases complained of naso-pharyngeal catarrh; this also resisted treatment till the patient was removed from work, when simple methods cleared up the condition. I have seen no cases which would lead me to say that those cases of system poisoning resulted in any permanent form of incapacity.

I have seen no cases in which jaundice was a complication, nor have I seen any cases where the anæmia was intractable.

The question of the effect on the teeth came up from time to time, and after sifting every case, I have seen no instance where the fact that they were working in an atmosphere of gases and vapours caused decay of sound teeth. On the other hand, evidence seems to show that in a tooth which was already diseased, the process of decay was more rapid. Operatives were warned in every case to pay special attention to the cleansing of their teeth.

Clothing of Workers.

Conditions met with in working with nitric acid are very hard on clothing, and it is desirable that the employer should provide special clothing for the workers.

Thick woollen cloth stands up to nitric acid work better than any other, whilst cotton goods are useless and dangerous. During the recent war reject army and police clothing proved very satisfactory.

For footwear, clogs with thick wood soles are much more serviceable than boots. Two points ought to be noted in regard to clogs in order to make them comfortable in wear, viz., the soles should be shaped to the natural lie of the foot, and they should be provided with supple leather tops as usually provided for boots. Tops taken from otherwise worn-out boots do very well for clogs.

Commercial Pure Nitric Acid.

Pure nitric acid is required only to a very limited extent, chiefly for chemical laboratory purposes. It may be prepared by redistillation, in glass or silica ware vessels at a low temperature, with selection of the middle portion of the distillate. For analytical acid, traces of haloid acids and sulphuric acid may be prevented from distilling by fixing these with silver nitrate and barium nitrate respectively. Dissolved lower oxides of nitrogen may be removed by blowing warmed air through the distillate.

USAGE OF NITRIC ACID.

United Kingdom.

The pre-war usage of nitric acid in the United Kingdom amounted to about 14,000 tons, reckoned as 100 per cent. HNO_3.

As a result of the growth of the synthetic dye industry, the usage in normal after-war periods may rise to about 30,000 tons.[1]

U.S.A.[2]

	1900. lb.	1905. lb.
Production . . .	63,084,722	108,308,387
Consumption :		
Dyestuffs . . .	1,703,160	663,585
Explosives . . .	35,353,600	82,676,800
Fine chemicals . .	183,667	1,505,870
General chemicals .	353,014	4,256,111
Parting metals . .	10,221,786	6,810,273
Plastics . . .	2,971,469	4,710,451
Refining metals . .	8,000,000	3,000,000
All other uses . .	4,297,826	4,757,297

COST OF PRODUCTION.

The pre-war cost of making concentrated (90 per cent.) nitric acid in Britain by the retort process, with Chili nitrate at £10, 5s. per ton and rectified sulphuric acid at £3 per ton, including fuel, labour, repairs, general expenses, amortisation and interest on capital, amounted to £22, 7s. per ton of HNO_3 (calculated as 100 per cent.) in the form of 90 per cent. nitric acid.

The average pre-war selling prices of 65 per cent. acid and 94 per cent. acid amounted respectively to about £21, 5s. and £24, 5s. per ton of HNO_3 (calculated as 100 per cent.).

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[1] *Cf.* Final Report, Nitrogen Products Committee.

[2] C. E. Munroe, *J. Washington Acad Sci.*, 1911, **1**, 70-73.

Very detailed costs accounts of war production are given in the Report on the Statistical Work of the Factories Branch of the Department of Explosives Supply.[1]

USES OF NITRIC ACID.

Nitric acid is used in the manufacture of:—

1. Sulphuric acid by the Chamber process.
2. Organic nitrates and nitro-bodies used in explosives, *e.g.*, gun-cotton, nitro-cotton, nitro-glycerine, picric acid, tri-nitro-toluol (T.N.T.), tetryl, etc.
3. Fulminates of mercury and silver for explosives.
4. Ammonium, barium, calcium, strontium, lead, etc., nitrates for explosives and fireworks.
5. Organic nitro-bodies for use in the manufacture of dyes, etc.
6. Nitro-cotton for celluloid, collodion, artificial silk, etc.
7. Ammonium and calcium nitrates.
8. Silver nitrate for photography.
9. Iron nitrate for mordanting.

Nitric acid is also used for etching copper, *e.g.*, for calico printing, engraving, etc., and in the separation of gold from silver, for assay purposes (parting).

The pure acid finds use in chemical laboratory practice.

USES OF NITRE CAKE.

Largely owing to the vital necessity for strict economy in the consumption of sulphuric acid during the recent war, every possible outlet for nitre cake as a substitute for sulphuric acid was closely examined (as a study of the patent literature clearly indicates), and most of these were made use of.

At the end of 1917 the distribution of nitre cake for use in the British Isles by the Government department responsible was as follows[2]:—

1. For grease recovery from the wash liquors of the textile industries	25 per cent.
2. For bleaching and dyeing	25 ,,
3. For metal pickling and cleaning	21 ,,
4. For hydrochloric acid manufacture	21 ,,
5. For mineral water manufacture	4 ,,
6. For miscellaneous purposes	4 ,,

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[1] H.M. Stationery Office, London, 1919.

[2] Calvert and Morris, *J. Soc. Chem. Ind.* (*Review*), 1920, **39**, 407-11.

The miscellaneous uses included :—

1. The manufacture of glue or manures from fleshings, hide scrap, leather dust, and leather scrap.
2. Glass making.
3. Rubber regeneration.
4. The process of glycerine production.
5. The manufacture of sodium bisulphate tablets for water sterilisation.
6. For fertilisers, including superphosphate and sulphate of ammonia.
7. The "striking out" of phenols.
8. The manufacture of Epsom salts.
9. Dissolving zinc and copper ores.
10. Fluxing in metal extraction.
11. The manufacture of hydrogen and sulphuretted hydrogen.
12. The preparation of tartaric acid substitutes.
13. Paper sizing.
14. Alum making.
15. Extraction of the rare earths.

The main pre-war use of nitre cake was in the production of salt-cake.

Transport of Nitric Acid.

The transport of nitric acid presents considerable difficulty owing to its extremely corrosive nature, to its ready decomposition with production of poisonous fumes, and to its power, when concentrated, of causing organic substances such as paper, straw, shavings, etc., to take fire.

The well-known glass carboy, packed with straw in iron hampers, is still the most usual container for nitric acid in transport. The safer earthenware carboy has the disadvantage of greater weight.

Lead, cast iron, and aluminium vessels, suitably mounted for road or rail, are used for the carriage of nitric acid between departments in a works, while for long distance transport aluminium vessels are used.

For the transport of nitric acid in bulk, advantage is often taken of the possibility of carrying a mixture of nitric and sulphuric acids in steel drums or tank wagons. Such mixtures may be used as such for nitration purposes, or for sulphuric acid manufacture, or the nitric acid can be recovered by distillation.

Railway Regulations.

1. **Nitric Acid or Aqua-fortis not exceeding 1·420 sp. gr.**—In glass carboys not exceeding 12 galls. in capacity.

2. **Traffic in Carboys**—STRAW PACKING.—Each carboy must be firmly packed in a hamper of iron or wickerwork, with a minimum thickness of ½ in. of straw packing between the hamper and the carboy. This packing must be renewed as soon as it loses its elasticity, and the hamper must be kept in good repair.

The straw packing in the carboy hampers must be sufficiently damp to prevent fire.

STOPPERING AND LUTING.—Each carboy must be provided with a good earthenware or glass stopper, and must either (*a*) be well luted with plastic (moist) clay, or (*b*) well luted first with plaster of Paris and then a layer of moist clay placed over the plaster of Paris, the stopper in all cases to be tied over with a waterproof material to keep the clay moist, and then with strong canvas firmly tied or wired round the neck of the carboy.

Other equally effective means of luting may be used, provided the stopper is in all cases firmly secured and luted, so that the acid cannot escape.

An effective method of securing the stopper is by means of a flat metal band, passing round the neck of the carboy and over the canvas, thus—

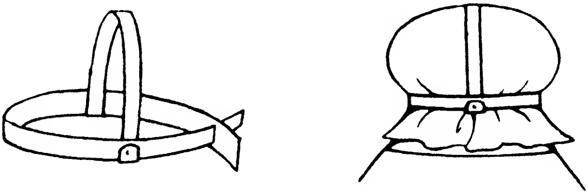

FIG. 99.—Method of Securing Carboy Stopper.

LOADING.—For traffic in full truck single tier loads, the carboys must be placed close up to the end and side of the wagon and fastened together at all points of contact with strong cord or wire; any space must either be battened off with substantial timber, positioned close to the shoulder of the carboys, or filled with other approved packing such as straw, sacks of straw, old hampers, etc., or alternatively, a framework approved by the Company may be fitted in the truck to support each carboy separately.

In the case of double tier loads each carboy must be placed on a nest of straw between the shoulders of the bottom tier carboys, the two rows of three at either end to be fastened together with strong cord or wire at each point of contact. The carboy hampers must be interlaced with rope, the ends of which must be braced to give firmness, and secured to the buffers or sheet hooks of the wagon. Wagons exceeding the height of the carboys must not be used.

Note.—The Great Western Railway Company do not carry nitric or sulphuric acid in double tier loads, and require the end hampers in single tier loads to be secured to the ends of the truck with strong cord fastened to the buffers or sheet hooks.

In the case of single carboys or part loads, the carboys and hampers must be packed in substantial flat-bottomed boxes, crates, or tubs. Each package must bear a label close to the mouth of the carboy:—

"THIS SIDE UP."

Carboys in boxes, crates, or tubs must not be loaded on the top of other goods, nor other goods loaded on the top of such carboys. Goods liable to be damaged in the event of breakage or leakage of the contents of the carboys must not be loaded near them.

3. **Nitric Acid or Aqua-fortis.**—In stoneware jars protected by wickerwork or iron hampers.

In bottles packed in cases or boxes. Each bottle must be completely surrounded with kieselguhr, whiting, or other material, on which the acid has no chemical action. The case or box must not contain any sawdust, straw, or other inflammable substance, but a piece of strong paper may be placed under the lid to prevent the escape of the packing material. Sulphuric acid, inflammable liquid, or other chemical which by contact with nitric acid might cause fire or explosion, must not be packed in the same case or box.

4. **Mixed Acids**—NITRIC AND SULPHURIC ACIDS, CONCENTRATED, MIXED, containing not less than 20 per cent. of sulphuric acid; the sp. gr. of the nitric acid to be not less than 1·42, and of the sulphuric acid not less than 1·84.—In approved steel drums. The gross weight per drum not to exceed 1400 lb. The drums not to be accepted unless in good condition and free from rust.

In owner's tank wagons, 8 tons per wagon. The manhole covers and other openings of these tanks must be closed water-tight, whether the tanks be loaded or empty. A written declaration must be obtained from the senders with each consignment that the acids have not been used in the manufacture of nitro-glycerine or other explosive.

DIPPING ACID (mixture of nitric and sulphuric acids, diluted).—In stoneware jars protected by wickerwork.

In glass carboys.

REFERENCES

Manufacture.

PRENTICE.—*J. Soc. Chem. Ind.*, 1894, **13**, 323.
GUTTMANN.—*Ibid.*, 1901, **20**, 5 ; 1908, **27**, 668 ; 1905, **24**, 1031.
WINTELER.—*Chem. Zeit.*, 1905, **29**, 820.
GUTTMANN.—*Ibid.*, p. 934.
WINTELER.—*Ibid.*, p. 1010.
VOLNEY.—*J. Amer. Chem. Soc.*, 1891, **13**, 246-51 ; 1901, **23**, 489-92 ; *J. Soc. Chem. Ind.*, 1901, **20**, 544-6 ; *cf.* also *J. Amer. Chem. Soc.*, 1902, **24**, 222-6 ; *J. Soc. Chem. Ind.*, 1901, **20**, 1189-91.
LUNGE.—*Z. angew. Chem.*, 1891, p. 167.
INOUÉ.—*Chem. Zeit. Rep.*, 1914, p. 399.
HART.—*Met. and Chem. Eng.*, 1918, **18**, 534-6.
SMITH.—*Gas World*, 1917, **67**, No. 1737, 16.
WALKER.—*J. Chem. Soc. Trans.*, 1920, **117**, 382-9.
HART.—*J. Amer. Chem. Soc.*, 1895, **17**, 576-84.
MAUGÉ (Valentiner Process).—*L'industrie chimique*, 1920, **7**, 105-8.
MAUGÉ (Uebel Process).—*Ibid.*, pp. 265-6.
BOTTOMLEY (fused silica plant for).—*J. Soc. Chem. Ind.*, 1917, **36**, 579.
PRANKE.—*J. Ind. Eng. Chem.*, 1918, **10**, 830-1.
PARSONS (comparison of cost of nitrate nitric acid and synthetic nitric acid).—*Chem. and Met. Eng.*, 15th May 1919.
WEBB.—*J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 212-20.

Chase.—*J. Ind. Eng. Chem.*, 1922, **14**, 677-81.
Zeisberg.—*Chem. and Met. Eng.*, 1921, **24**, 443-5.
Crawford.—*J. Soc. Chem. Ind.* (*Trans.*), 1922, **41**, 321-4.
The Manufacture of Nitric Acid from Nitre and Sulphuric Acid; "Technical Records of Explosives Supply, 1915-18, No. 7, H.M. Stationery Office."
Marshall.—"Explosives."
Guttmann.—"The Manufacture of Explosives."

Iodine in Nitric Acid.

White.—*J. Soc. Afr. Assoc. Anal. Chem.*, 1919, **2**, 7-12; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, **38**, 795.

Cements and Lutes.

Sadtler.—*Chem. Trade J.*, **84**, 517.

Absorption.

Lewis and Edgar.—*J. Amer. Chem. Soc.*, 1901, **23**, 1330.
Lewis and Edgar.—*Ibid.*, 1911, **33**, 292.
Lunge and Berl.—*Z. angew Chem.*, 1906, **19**, 807.
Lunge and Berl.—*Ibid.*, 1907, **20**, 2074.
Foerster and Koch.—*Ibid.*, 1908, **21**, 2161, 2209.
Bodenstein.—*Ibid.*, 1909, **22**, 1153.
Partington and Parker.—*J. Soc. Chem. Ind.* (*Trans.*), 1919, **38**, 75-80.
Knox and Reid.—*Ibid.*, p. 105.
Geake and Squire.—*Ibid.*, pp. 367-9.
Sanfourche.—*Comptes rend.*, 1919, **168**, 401-4; *J. Chem. Soc. Abstr.*, 1919, **116**; [II], 150.
Schellhaas.—*Chem. Zeit.*, 1920, **44**, 122-3; *J. Amer. Chem. Soc.* (*Abstr.*), 1920, **14**, 2054.
Rideal.—*J. Ind. Eng. Chem.*, 1920, **12**, 531-8; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, **39**, 514.
Foerster, Burchardt, and Fricke.—*Z. angew. Chem.*, 1920, **33** [I], 113-7, 122-7, 129-32; *J. Amer. Chem. Soc.* (*Abstr.*), 1920, **14**, 2395.
Burdick and Freed.—*J. Amer. Chem. Soc.*, 1921, **43**, 518-30.
Burdick.—*Ibid.*, 1922, **44**, 244-51.
Burdick.—*J. Ind. Eng. Chem.*, 1922, **14**, 308-10.

Packing for Towers.

Zeisberg.—*Chem. and Met. Eng.*, 1919, **21**, 765-7.
Wyld and Shepherd.—B. P. 839 of 1915.

Concentration.

Creighton and Smith.—*J. Franklin Inst.*, 1915, **180**, 703-9; *J. Chem. Soc. Abstr.*, 1916, **110**; [II], 97.
Kaltenbach.—*Chimie et Industrie*, 1919, **2**, 142-52; 1920, **4**, 576-90; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, **39**, 655.

Foerster, Burchardt, and Fricke.—*Z. angew. Chem.*, 1920, **33**, 113-7, 122-7, 129-32 ; *J. Chem. Soc. Abstr.*, 1921, **120** ; [II], 162.

Galle.—*Z. angew. Chem.*, 1921, **34**, 168-70, 173-5 ; *J. Soc. Chem. Ind.* (*Abstr.*), 1921, **40**, 385.

Creighton.—*J. Franklin Inst.*, 1922, **193**, 89-95.

Carpenter and Babor, *Chem. and Met. Eng.*, 1922, **26**, 443-4 ; *ibid.*, p. 871 ; *ibid.*, 1922, **27**, 121-4.

Fume Poisoning.

Lehmann and Diem.—*Arch. Hygiene*, 1913, **77**, 311-22 ; *J. Chem. Soc. Abstr.*, 1913 ; [I], **104**, 320.

Lehmann and Hasegawa.—*Arch. Hygiene*, 1913, **77**, 323-68 ; *J. Chem. Soc. Abstr.*, 1913 ; [I], **104**, 320.

L. A. De Blois.—National Safety Council, Chem. Section, Detroit, Oct. 1916 ; *J. Ind. Eng. Chem.*, 1916, **8**, 1162-3 ; *J. Soc. Chem. Ind.*, 1917, **36**, 44.

Zadeck.—*Berl. klin. Wochenschr.*, **53**, 246-50 ; *Chem. Zentr.*, 1916, **1**, 990 ; *J. Amer. Chem. Soc.* (*Abstr.*), 1918, **12**, 66.

54th Annual Report on Alkali, etc., Works, 1917.—*J. Soc. Chem. Ind.* (*Review*), 1918, **37**, 306.

Rambousek.—“ Industrial Poisoning ” (1913).

Fieldner, Teague, and Yoe.—*J. Ind. Eng. Chem.*, 1919, **11**, 622-3.

Levy and West.—*J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 234-7.

Berl and Samtleben.—*Z. angew. Chem.*, 1922, **35**, 201-2, 206-11.

Nitre Cake.

SOLUBILITY.

Foote.—*J. Ind. Eng. Chem.*, 1918, **10**, 896-7 ; *J. Chem. Soc. Abstr.*, 1919, **116**; [II], 24.

CRYSTALLISATION.

Dawson.—*J. Chem. Soc. Trans.*, 1918, **113**, 675-88.

Saxton.—*J. Ind. Eng. Chem.*, 1918, **10**, 897-901 ; *J. Chem. Soc. Abstr.*, 1919, **116** ; [II], 24.

CONSTITUTION.

Butler and Dunnicliff.—*J. Chem. Soc. Trans.*, 1920, **117**, 666.

UTILISATION OF NITRE CAKE.

For Fertilisers.

54th Annual Report on Alkali, etc., Works.—*J. Soc. Chem. Ind.* (*Abstr.*), 1918, **37**, 522.

Dawson.—*J. Chem. Soc. Trans.*, 1918, **113**, 675-88 ; (digest in *J. Soc. Chem. Ind.* (*Abstr.*), 1918, **37**, 577).

Parrish.—*Gas J.*, 1918, **143**, 395-6 ; *J. Soc. Chem. Ind.* (*Abstr.*), 1918, **37**, 577.

Brioux.—*Comptes rend. acad. agr. France*, 1918, **4**, 632-8 ; *J. Amer. Chem. Soc.* (*Abstr.*), 1918, **12**, 2104.

Anon.—*Chem. Trade J.*, 1918, **63**, 25.

SHUTT AND WRIGHT.—*Canadian Chem. J.*, 1918, **2**, 314-6; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, **38**, 85.

FISCHER AND NIGGEMANN.—*Chem. Zentr.*, 1919; [II], **90**, 559; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, **38**, 532.

DAWSON.—*J. Soc. Chem. Ind.* (*Trans.*), 1919, **38**, 98-101.

NEUMANN AND KLEYLEIN.—*Z. angew. Chem.*, 1920, **33**, 74-7; *J. Amer. Chem. Soc.* (*Abstr.*), 1920, **14**, 3492.

For Pickling Metals.

BROWNSDEN.—*J. Soc. Chem. Ind.*, 1917, **36**, 575.

KILBURN SCOTT.—*Ibid.*, pp. 810-2.

For Glass Manufacture.

SPRINGER.—*Ker. Rundschau*, 1917, **25**, 67; *J. Soc. Glass Tech.* (*Abstr.*), 1918, **2**, 53; *J. Amer. Chem. Soc.* (*Abstr.*), 1918, **12**, 2672.

MORGAN.—*Econ. Proc. Roy. Dublin Soc.*, 1917, **2**, 238-47; *J. Soc. Chem. Ind.*, 1917, **36**, 504.

For Paper Industry.

STEPHENSON.—*J. Soc. Chem. Ind.* (*Trans.*), 1918, **37**, 128.

For Salt Cake.

GROSSMANN.—*J. Soc. Chem. Ind.*, 1917, **36**, 1035-8; *J. Soc. Chem. Ind.* (*Trans.*), 1918, **37**, 103-4.

GOODWIN.—*J. Soc. Chem. Ind.*, 1917, **36**, 1161.

GODBER.—*J. Soc. Chem. Ind.* (*Trans.*), 1918, **37**, 48.

General.

PILZ.—*Zeitschr. f. landw. Versuchswesen, Österr.*, 1918, **21**, 613-23; *Centr. Bakteriol. Parasitik*, **50**, 186; *J. Amer. Chem. Soc.* (*Abstr.*), 1920. **14**, 3744.

MOSCICKI AND DOMINIK.—*Pzremysl Chem.*, 1920, **4**, 17-23; *Chem. Zentr.*, 1920; [IV], **91**, 430; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, **39**, 746.

CHURCHILL.—*J. Amer. Leather Assocn.*, **13**, 607; *J. Amer. Chem. Soc.* (*Abstr.*), 1919, **13**, 673.

SABALITSCHKA.—*Ber.*, 1919, **52**, 567-84.

CORBETT.—*Bureau of Mines*, Oct. 1918, 17 pp.; *J. Amer. Chem. Soc.* (*Abstr.*), 1919, **13**, 221.

BASSETT.—*Chem. and Met. Eng.*, 1918, **19**, 790.

HART.—*J. Ind. Eng. Chem.*, 1918, **10**, 238.

JOHNSTON.—*Ibid.*, pp. 468-71.

(DISCUSSION).—*J. Soc. Chem. Ind.*, 1917, **36**, 1216*a*-1216*b*.

BERL, DEFRIS AND VON BOLTENSTEIN.—*Z. angew. Chem.*, 1921, **34**, 517.

PATENTS

Manufacture.

Valentiner and Schwarz (Fr. P. 374902 and U.S. P. 920224), in the manufacture of nitric acid under diminished pressure, restrict the passage between the retort and the condensing coil to half the diameter of that coil. The higher pressure thus maintained in the retort prevents the uprush of sodium nitrate through the superincumbent sulphuric acid, which causes the distillation to progress more rapidly. The condensing coil extends to the bottom of the first of a series of receivers, so as to form a liquid seal, and gases such as lower nitrogen oxides and HCl pass on, leaving pure nitric acid behind.

Valentiner (B. Ps. 610 of 1892 and 19192 of 1895).

Dreyfus (B. P. 13826 of 1895). Vacuum process.

Valentiner and Schwarz (Ger. P. 144633) explain why pure 100 per cent. nitric acid up to that time had not been obtained in one operation as due to the difficulty of decomposing sodium nitrate by sulphuric acid of 170° Tw. in the vacuum on a manufacturing scale, owing to the formation of enormous quantities of froth towards the middle of the operation, which is perilous for the stoneware parts of the apparatus and contaminates the distilling acid with bisulphate carried over. This frothing can be avoided by adding the sulphuric acid not all at a time. The retort is charged with the nitrate and with about one-third of the sulphuric acid (170° Tw.) required for complete decomposition; this quantity is completely mechanically absorbed by the nitre. The evolution of nitric acid commences immediately, and when the boiling temperature has been attained, the nitric acid begins to distil off quietly and evenly. According to the progress of distillation, fresh sulphuric acid is run into the retort, at such a rate that there is always enough sulphuric acid present to decompose the nitrate into bisulphate and nitric acid. The sulphuric acid is run into the retort neck through a vessel, filled with pumice blocks, through which the nitric acid vapours must pass before leaving the retort, by which process they are completely purified and concentrated. The fresh sulphuric acid, run through that pumice vessel on to the nitre, acts much better than that acid which has been in the retort for hours and is charged with bisulphate, since that fresh acid contains no bisulphate in solution.

Glock (Ger. P. 110254) heats nitrate in a pan provided with stirring-gear to 120° to 150° and runs in the equivalent quantity of sulphuric acid, previously heated to 100° to 130°, in a thin jet. The end of the decomposition is facilitated by steam or a thin jet of water. At last air is blown through, whereupon the solid, pulverulent neutral sodium sulphate is ladled out. Or else the nitrate is from the first heated to 250° C.

Manufacture of Nitric Acid without Sulphuric Acid.—Campbell and Walker (B. P. 9782 of 1894) grind nitre cake with nitrate of soda and charge the mixture into retorts provided with a mechanical agitator.

Garroway[1] (B. P. 6777 of 1899) mixes ordinary acid nitre cake with sodium nitrate, heats the mixture in a retort, and blows a spray of weak nitric acid by means of compressed air over the mixture. The nitrogen oxides, mixed with steam and air, are regenerated by condensing-tubes and towers into nitric acid. It is alleged that ultimately a 96 per cent. acid can be produced. The residue is neutral salt-cake, testing 98.36 per cent.

Garroway (B. P. 2466 of 1895) also prepares nitric acid by heating a mixture of nitrate of soda and ferrous sulphate or alum, obtaining sulphate of soda and oxide of iron or alumina. He also patents the decomposition of sodium nitrate by silica (B. P. 2489 of 1896).

A special retort for the Lunge and Lyte process (decomposition of $NaNO_3$ by Fe_2O_3) has been constructed and patented (Ger. P. 90654). It consists of a revolving cylinder placed in a sloping position, with inner projections and contrivances for feeding and exhausting without stopping the process. A full description of the whole process has been given by J. L. F. Vogel.[2]

Main, Stevenston, and M'Donald (B. P. 23819 of 1895) heat sodium nitrate with manganese oxides. Garroway (Ger. P. 79699) employs lime and superheated steam. Vogt (B. P. 22018 of 1891) heats with lime, ferric or manganese oxides in a current of superheated steam and carbon dioxide.

Hemingway (U.S. P. 781826) manufactures nitric acid by mixing nitrate of soda, sulphuric acid, and water, heating the mixture to 77° and gradually adding ferrous sulphate. Ferric sulphate and sulphate of soda are obtained as by-products. The nitrous vapours are condensed in the usual manner with the admixture of air.

Blackmore (for Robinson and Spruance, U.S. P. 982466) exposes barium nitrate to the action of superheated steam, whereby BaO_2 and nitric acid are formed.

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[1] *J. Soc. Chem. Ind.*, 1901, p. 1191.

[2] *Eng. and Min. J.*, 1900, p. 408.

The Chemische Werke vorm. Byk (Ger. P. 208143) make concentrated nitric acid from calcium nitrate by adding concentrated sulphuric acid, and separating the liquid from the $CaSO_4$ formed by filtering, pressing, or centrifuging. The same process is described in the U.S. P. 928545. According to Ger. P. 217476 they bring about the decomposition of the calcium nitrate by the theoretical quantity of sulphuric acid in the presence of so much water that nitric acid of not essentially more than 59 per cent. HNO_3 is formed. The advantage of this modification is that the time of filtration is very much reduced, as hydrated calcium sulphate allows the liquid to pass through rapidly, and the channels are not stopped up by the hydration. Moreover, more concentrated nitric acid is thus obtained for a given concentration of sulphuric acid, because the gypsum combines with 2 mols. of water. They dissolve 100 parts of Notodden nitre in nitric acid of 55° B. and add sulphuric acid until no more calcium sulphate is precipitated (Fr. P. 400305).

F. W. de Jahn (U.S. P. 1023138, transferred to the General Chemical Company) agitates sodium nitrate with sulphuric acid under diminished atmospheric pressure at a temperature below the fusing-point of the bisulphate formed, preferably below 384 F. (195° C.).

F. W. de Jahn and the General Chemical Company (Ger. P. 252374; U.S. P. 1023133) effect the decomposition of nitrates by sulphuric acid under diminished pressure at lower temperatures, and in a short time by constantly agitating the mass, and avoiding the fusion of the bisulphate formed. The best temperature is 135°, and in the end the vacuum is brought to 28 in.

Chatfield (B. P. 16512, 1891) employs a large excess of sulphuric acid for decomposing the nitrate, in order to obtain a residue easily fusible at the temperature of reaction, which may be utilised for the production of hydrochloric acid, etc.

J. F. White (U.S. P. 648322) collects the weak nitric acid distilling at first by itself, and adds it to the next charge of nitrate and sulphuric acid.

Claessen (B. P. 6102, 1915; Ger. P. 287795) puts the nitre, with addition of a little sulphuric acid or nitre cake, through a briquetting machine, in order to obtain cubes of about an inch diameter, which are worked in the nitric acid retorts much more easily than powdered nitrate.

The Du Pont de Nemours Powder Co. (U.S. P. of Beers, Nos. 1240351 and 1149711) heats the now frequently employed large-sized nitric acid retorts by means of an oil-bath, whereby a high yield and economy of fuel are attained.

Valentiner (Ger. P. 63207; B. P. 4254, 1907; Aust. P. 36792; Fr. P. 374902; U.S. P. 920224). Vacuum process.

Volz (U.S. P. 500785). Vacuum process.

Traine and Hellmers, Wever and Brandenburg (Ger. P. 269656) prepare nitric acid by heating calcium nitrate, treating the evolved gases with moist oxygen or moist air, and adding before or during the introduction of fresh calcium nitrate into the heating apparatus a sufficient quantity of indifferent, difficultly fusing material, in order to cause the fluxing mass not to come into direct contact with the hot walls of the apparatus, but to be enclosed and absorbed by the newly added material, which prevents or at least lessens the caking up of the fluxed calcium nitrate and its adhesion to the sides of the apparatus.

W. Mills (U.S. P. 755378) dissolves substances containing lead in hydrofluosilicic acid, treats the solution with an alkaline or earthy alkaline nitrate, and decomposes the plumbic nitrate formed thereby by sulphuric acid.

Baynes and the Chemical and Electrolytic Syndicate, of London (B. P. 7273, of 1895; U.S. P. 632394), prepare nitric acid continuously by heating a mixture of alkaline nitrate with ferric oxide in a thin layer, in a retort into which air or a mixture of air and steam is introduced.

The Société anonyme des Poudres et Nitrates (Fr. P. 473433) heats a mixture of potassium or sodium nitrate with alumina or bauxite in a current of superheated steam to 250 to 400°, and lixiviates the residue with water, in order to obtain a solution of alkali aluminate. The reaction is prompted by adding 10 per cent. of calcium nitrate, and fusion is prevented by the addition of 10 to 15 per cent. alkali aluminate from a previous operation. A barium or strontium compound may be added, in order to convert the silica into an insoluble silico-aluminate.

According to their Ger. P. appl. S42945, to the mixture of nitrate and alumina 10 per cent. calcium carbonate is added, in order to keep the mass in a porous state, and the mixture is moulded into briquettes, which are treated as above.

Nodon (Ger. P. 274346) obtains nitric acid immediately from the natural saltpetre earths, *e.g.*, peat, by electrolysis. He places in the nitre-bearing soil porous vessels containing dilute nitric acid and coke, which serve as an anode. The nitric acid obtained by the electrolysis of the nitrate contained in the soil collects in these vessels; the alkalies or alkaline earths, formed by the electrolysis, migrate to the cathodes, which consist of cast iron or sheet-iron plates sunk in the nitre pits. The Joule heat developed by the current is utilised for keeping up an even temperature favourable for the reaction. According to one of the patent claims, the peat soil is kept alkaline by placing lime or calcium carbonate between the anodes and the soil. The floor of the peat moor has an electric resistance of about 3 ohms per cubic metre. The electric current has about 10 volts; it produces at the anode nitric acid, at the cathode lime. Many details on the process are given in the patent description. The process is described at length by Dary.[1]

The Oesterreichische Verein für chemische und metallurgische Produktion at Aussig (Ger. P. 280967) prepares nitric acid by heating ammonium nitrate with so much sulphuric acid that it suffices at least for producing ammonium hydrosulphate. This allows of driving off the nitric acid completely at temperatures not much above 120°, and is finished up to 152°. If less sulphuric acid is employed, losses are caused by the necessity of working at higher temperatures, whereby the ammonium nitrate is decomposed. The residue from the distillation, after being neutralised by sulphuric acid, furnishes saleable ammonium sulphate. By this process pure nitric acid can be prepared from the impure dilute acid obtained by the oxidation of atmospheric nitrogen.

Frischer (B. P. 7099, 11th May 1915). Retorts for the distillation of volatile acids, *e.g.*, nitric acid, are provided with a number of pipes at different points for carrying off the acid vapours. These pipes are connected singly or in pairs to separate condensers which unite towards the end of the cooling system. A more rapid, uniform, and economical distillation results, and larger retorts can be used, *e.g.*, 5000 kilos of saltpetre can be treated in six to eight hours.

Tentelev Chem. Works (B. P. 110637, 21st November 1916). Pure nitric acid is obtained by distilling concentrated nitric acid with a solution of a suitable nitrate such as zinc or nickel nitrate. The nitric acid is gradually introduced into the nitrate solution which is maintained at a suitable temperature (126° to 170° C. or more being mentioned). The rate of introduction of the crude acid is regulated so as to be about equal to the rate of distillation. The strength of the pure acid may be regulated by selecting different concentrations of the nitrate solution.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Norw. P. 27550, 15th January 1917). Ammonium nitrate is distilled with sulphuric acid at a pressure less than 1 atmosphere, and in the proportion of less than 2 mols. acid to 1 mol. nitrate.

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[1] *Chem. Trade J.*, 1914, 54, 75 *et seq.*

Bayer (Ger. P. 301702, 19th April 1917). By connecting a series of retorts by means of pipes to equalise the pressures and charging the retorts at regular intervals, uniformity of the process is ensured.

Maxted and Smith (B. P. 126704, 26th April 1917). Nitric acid of high concentration is obtained by the reaction of water, excess of oxygen, and large excess of liquid NO_2 or N_2O_3 at pressures not appreciably exceeding atmospheric, the excess of lower oxide being subsequently expelled for instance by a current of air or by gently heating, but without separating the separate layers when such layers form.

Manser (U.S. P. 1320080, 28th October 1919). A hollow conical spreader is placed within the still at its bottom provided with inlet openings at its lower edge and a protected gas outlet at its upper end. The still is specially adapted for distilling nitric acid from sodium nitrate and sulphuric acid.

Banigan (U.S. P. 1332195, 2nd March 1920). A mixture of pulverised nitre cake and sodium nitrate is passed in a stream through a rotating tubular retort continuously while subjected to a tumbling movement. Near the discharge end of the stream a higher temperature is maintained than near the inlet end of the apparatus. Nitric acid produced is caused to flow in a direction opposite to the travel of the stream.

Tayntor (U.S. P. 1361416, 7th December 1920). A plant for manufacture of nitric acid from sodium nitrate and sulphuric acid is so constructed that all the stills of a 20-still acid house are provided with a common expansion chamber with five bleachers, to which the common expansion chamber delivers. Condensers from the bleachers deliver to a common chamber to receive uncondensed gas, adapted to deliver to a tower house. This arrangement equalises pressure and facilitates uniform operation.

W. Strzoda (Ger. P. 330019, 13th October 1917; addn. to 272158). The apparatus, constructed from brittle material cemented and strengthened as described in the chief patent (*cf.* B. P. 26732 of 1913), is arranged to provide the maximum reaction surface and area of the gas channels in proportion to the diameter of the tubes. The gas channels, which are of circular cross-section, are arranged around a central overflow tube, and are covered with annular hoods fitted with overflow dishes.

Continuous Manufacture.

Prentice (B. P. 6960 of 1893; Ger. P. 79645; B. P. 8902 of 1893).

Chemische Fabrik Rhenania (B. P. 27240 of 1898; B. P. 3305 of 1901). Uebel process.

The Badische Anilin- und Sodafabrik (Ger. P. 227377) manufacture nitric acid in a continuous way. The mixture of sodium nitrate and sulphuric acid passes through a series of stills which are heated each by itself to various degrees, and in which the contents are kept in mechanical motion. The outlet pipes for the vapours are shaped as siphons, and the vapours are separately condensed. With a series of five stills, the temperatures and strengths of acid, etc., are as follows:—

	Temperature. Degrees.	Strength of acid.	
Still No. 1 .	110 to 120	96 to 97 per cent.	(60 per cent. of the total acid).
,, 2 .	150 ,, 170	88 ,, 90 ,,	
,, 3 .	210 ,, 250	60 ,,	
,, 4 .	250 ,, 280	2 ,, 5 ,,	
,, 5 .	280 ,, 300		

Schellhaass (Ger. P. 241711) also makes nitric acid in a continuous way. Sulphuric acid and fused nitrate of soda are separately introduced as a spray into a tower-like retort, kept at a temperature of 180°. In this retort the materials float about and are thoroughly mixed, so that the reaction is quite complete. Nitric acid of high concentration distils over, and the sodium bisulphate, which contains some nitric acid, is collected in a second retort, heated to about 300°, from which a more dilute nitric acid distils off.

Chemische Fabrik Rhenania (Ger. Ps. 106962 and 127647). Uebel process.

The style of working of the Uebel process has been improved by further patents. According to Uebel's B.P. 19881, 1913 (Ger. Ps. 261874 and 277092; Fr. P. 461452; U.S. P. 1141994), the whole of the sulphuric acid required for decomposing the nitrate is at first only mixed with part of the charge of nitrate in the still and heated to 140°, at which temperature the whole of the nitrate introduced is decomposed, yielding highly concentrated nitric acid (phase 1); then the remainder of the nitrate is introduced, and its complete decomposition effected by raising the heat to 160° to 170° (phase 2). In the first phase the nitrate and the sulphuric acid can be introduced at the same time and gradually, so that there is always an excess of sulphuric acid; and in the second phase the nitrate, without sulphuric acid, is also gradually introduced. In this phase the mixture is heated to such a temperature that only concentrated nitric acid distils over; the residual mass is heated in another place to 250°, in order to drive out the water and the last portions of nitric acid. This process avoids the drawback of the ordinary process, that crusts are formed at the bottom which lead to frothing over, to explosive gas-developments, and to losses of nitric acid. The new process effects the production of highly concentrated nitric acid, gives a very even distillation, is very hygienic to work, free from danger, and gives an increase of production, as the stills have not to be allowed to cool down from one charge to the other.

Badische Anilin- und Sodafabrik (Fr. P. 406969).

Raschig (Ger. P. 283212) runs a paste of nitre and sulphuric acid continuously through a barometric tube at least 20 ft. long, into one end of a vacuum pan heated up to 170°, where the nitric acid is evolved as vapour. It is condensed in a stoneware cooler, and runs off through a barometric tube 23 ft. long. The liquid bisulphate passes at the other end of the pan again into a barometric tube 20 ft. long, and issues in the open air. The B. Ps. are Nos. 3208 and 13842, 1914; U.S. P. No. 1130104.

Hill and Moyler (U.S. P. 1362418, 14th December 1920). Nitric acid is made continuously by maintaining a flow of hot sulphuric acid, gradually merging into a flow of molten sulphates, distributing alkali metal nitrate on the surface of the sulphuric acid at a point in its flow and withdrawing nitric acid vapours at a point nearer the origin of the acid flow. An apparatus is described.

Condensation.

Trobridge (B. P. 25435 of 1906) protects earthenware pipes, used in the manufacture of nitric acid, from fracture by cold water by surrounding each vertical pipe from the bottom of the condensing tank to near the top, by a lead pipe about an inch wider than the earthenware pipe.

Ostwald (Ger. P. 207154) conveys hot nitrogen oxides in pipes made of nickel steel, but care must be taken lest any condensations take place, as nickel steel resists only *gaseous* nitrogen oxides.

A nitric-acid condenser, consisting of sets of perpendicular water-cooled pipes, is described in the B. P. 24332 of 1903, by Donnachie.[1]

Guttmann (B. P. 8915 of 1890; Ger. P. 73421; B. P. 18189 of 1897; B. P. 13694 of 1901; Ger. P. 160709).

Bate and Orme have patented an improvement of Guttmann's "water-battery" (B. P. 25790, 24th November 1902), the object of which is to ensure more efficient circulation of the condensing water.

Hart (B. P. 17289 of 1894).

Martin Kalbfleisch Co. (Ger. Ps. 104357 and 105704; Fr. P. 271025; U.S. P. 603402). Skoglund's condenser.

Niedenführ (Ger. P. 155095), in order to obtain the nitric acid

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[1] *Chem. Trade J.*, 1904, **35**, 380.

free from the lower nitrogen oxides, condenses it at a high temperature and with application of draught. The fan serving as draught producer is placed behind the condensing-receivers, and in front of the apparatus for oxidising and condensing the lower nitrogen oxides. Thus there is a slight lowering of pressure in the first condensers, by which the nitric acid is obtained in a purer state, and a rather higher pressure in the last part, which favours the oxidation going on there. Between the first condensers and the draught apparatus a cooler is interposed by which the draught apparatus is better protected against the action of the acid gases, and which also facilitates keeping the oxidising apparatus at a low temperature. His B. P. 4353 of 1905 describes the same process, and also a modification by which the conversion of the lower oxides of nitrogen into nitric acid is effected in two plate-towers, the first of which is rinsed only moderately so as to produce an acid of high strength, while the second tower is strongly rinsed, without regard to the strength of the acid obtained, which acid may be employed for rinsing the first tower.

Nathan, J. M. Thomson, and W. T. Thomson (Fr. P. 406806) condense nitric acid vapours by passing them through cooling-worms from the bottom upwards, the cooling being effected by running water on to the top of the coils. The upper ends of these are connected with a vacuum. The nitric acid running out at the bottom is almost free of lower nitrogen oxides.

Leblanc (Fr. P. 462712) passes the vapours through glass tubes, cooled inside by means of concentric pipes, and outside. Hough (B. P. 101307, 1916) also describes a tubular apparatus for that purpose.

The Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Fr. P. 451812) employs for cooling, condensing, and carrying nitric acid, vessels made of aluminium. These can be employed for acid containing less than 65 per cent. HNO_3, and not above 5 per cent. nitrogen oxides.

Hough (U.S. P. 1291893, 21st January 1919). The apparatus is similar in form to that described in B. P. 101307 of 1916,[1] but the condenser units consist of straight tubes, closed at the lower end and with lips at their upper ends; glass tubes connected with inlet and outlet leaders by flexible tubing are arranged within the condenser tubes, extending from a short distance above the bottom to above the lip at the upper end.

Hough (U.S. P. 1312118, 5th August 1919).

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[1] See *J. Soc. Chem. Ind.*, 1916, p. 1108.

Hough (U.S. P. 1326267, 30th December 1919). A vertical sectional casing contains a number of pipes arranged transversely, one above the other, and joined at adjacent ends—the joints being outside the casing—to form a continuous zigzag channel for the passage of the acid vapour. Inlet and outlet pipes for the cooling fluid are provided at the top and bottom of the casing, in which baffles are also disposed to compel the cooling fluid to traverse a tortuous path.

Bleaching.

Hirsch (Ger. P. 46096) runs the impure acid through a stoneware worm, placed in water of 80° C. Air is blown in at the bottom, and the feed of nitric acid is so regulated that it runs out at the bottom at a temperature of 60° C. and sufficiently bleached. It runs through a second worm placed in cold water, and can then be put into the carboys. The nitrous gases escaping at the top of the first worm are treated in the usual manner. One worm can purify several tons of acid per diem. The same process may also serve for treating the waste acid of nitroglycerine and nitrobenzene works; in this case air heated to 150° C. or steam is blown in at the bottom, and the feed of acid is so regulated that it issues, at a temperature of 140° C., as comparatively pure sulphuric acid.

The Chemische Fabrik Griesheim (Ger. P. 59099) places behind the retort a reflux-cooler, consisting of a Rohrmann stoneware worm contained in a water-tub kept at about 60 C. by the heat of the operation itself. The acid vapours ascending in this cooler are partially condensed there; in consequence of the high temperature the lower nitrogen oxides (together with the chlorine) escape in the state of vapour, and are condensed by air and water in a "Lunge tower" (plate-column) to weak nitric acid. The acid condensing in the worm flows into a receiver, kept at 80 C., and is therefore perfectly pure, no "bleaching" being required. Air is advantageously introduced into the receiver.

Moore and Hall (B. P. 28892 of 1910) avoid the absorption of lower nitrogen oxides in the condensation of nitric acid by passing the vapours upwards between cooled tubes, in such manner that the liquid formed on running down over these tubes gets sufficiently heated to avoid the absorption of the lower oxides. Further intimate contact of the liquid with the hot vapours is attained in a chamber, provided with partitions and filled with pumice, etc.

Casman (B. P. 11296, 1913; Fr. P. 457800) passes through the heated nitric acid a strong current of air, in order to oxidise the lower nitrogen oxides into tetroxide, and to drive this out; the N_2O_4 is subsequently oxidised into nitric acid by bringing it into contact with steam and a further supply of air.

Absorption.

For such purposes it is sometimes necessary to combine several plate-towers in sets, one tower being placed higher than the others and delivering its weak acid to those lower ones, to be got up to strength (Rohrmann and Niedenfuhr, B. P. 29746 of 1897).

Dawson (B. P. 123344, 14th November 1917). In the manufacture of nitric acid the gases from the condensers are treated in an empty tower with a spray of air and water produced by admitting compressed air by a nozzle opening below the level of the water in the bottom of the tower.

Dawson (B. P. 120869, 4th September 1918). In the absorption of nitrogen oxides in an upward spray of water and air in an empty tower in which the spray is produced by a jet of compressed air opening below the surface of the water in the bottom of the tower, the jet is surrounded by an inverted funnel having holes, the upper part of the funnel being above the level of the water. This arrangement prevents irregularities in the working of the jet owing to variations in the level of the water.

Concentration.

Colin (Fr. P. 211045) prepares fuming nitric acid of sp. gr. 1.5 by distilling nitric acid of 1.4 with sulphuric acid of 1.84 in enamelled cast-iron retorts, and employing a glass three-way cock for separating the distillates.

Erouard (Ger. P. 62714) also concentrates dilute nitric acid, or waste acids from nitrating processes, by adding strong sulphuric acid, or a solution of $CaCl_2$ or $MgCl_2$ [!], and distilling the mixture in a vessel in which it travels in a zigzag direction.

H. A. Frasch (Ger. P. 82578) prepares highly concentrated nitric acid by passing the vapours from the nitric-acid retort through a tower heated above the boiling-point of the acid, in which hot concentrated sulphuric acid is descending, or in which other dehydrating substances, such as anhydrous sulphate of soda or burnt plaster of Paris, act upon the mixed vapours.

The Verein Chemischer Fabriken in Mannheim (Ger. P. 85042) places between the still and the condenser, a dephlegmator, from which the dilute acid condensed there runs back into the still. This dephlegmator is kept at a temperature of 85° C., so that the concentrated acid can pass on.

Waldbauer (Ger. P. 155006), in order to avoid the expensive vessels used for distilling crude nitric acid, made of glass, porcelain, or platinum, or of running the impure acid into hot sulphuric acid (whereby the vessels are gradually attacked), fills the stills with some granular material, such as sand, pebbles, broken glass or china, preferably placing fine sand next to the sides of the vessel, then coarse sand, and in the centre pebbles. The acid is run upon the latter, gradually flows into the hotter parts near the sides, and is evaporated before it reaches the walls of the still. This process admits of employing stills made of a cheap and durable material, which could not be employed if the acid came into direct contact with it.

Collet (Norw. P. 13925; *Chem. Zeit.*, 1905, p. 457; U.S. P. 854928; Fr. P. 357221) concentrates nitric acid by means of hot air. The escaping gases and vapours are passed through a column fed with dilute nitric acid, then through a cooling-shaft, and at last through a vessel filled with lumps of calcium oxide. By this method it is claimed that 60 per cent. nitric acid is made more cheaply than by any other method.

Dieffenbach (Ger. P. 174736; Fr. P. 371688) also concentrates dilute nitric acid by heating it with alkaline polysulphates which take up the water, from which they can be again separated by heating by themselves. This may be done in cast-iron vessels without any visible damage to them. If 100 grams nitric acid of 36° B. is heated with 1000 grams polysulphate of the composition $NaHSO_4 : H_2SO_4$ to 105° to 120°, nearly all the nitric acid distils off with 95 per cent. HNO_3, and the remaining polysulphate is easily concentrated again [?].

Boeters and Wolffenstein (Ger. Ps. 189865 and 191912) heat nitric acid of, say, 68 per cent., in an iron retort and pass the vapours through a series of stoneware receivers, kept at about 100° by a water- or sand-bath, which are charged with a dehydrated nitrate. When this has taken up enough water, the receiver in question is put out of series by means of a three-way tap and is connected with a vacuum, whereby the nitrate is dehydrated and made again fit for use.

The same inventors (Fr. P. 371797) concentrate nitric acid by pouring it over calcium nitrate, dehydrated at 150° to 200°, which thereby passes over into a porous mass. Preferably, a counter-current is employed, if necessary with admission of air. For the concentration up to acid of 63 per cent. 1.25 to 1.5 parts of $Ca(NO_3)_2$ is required.

Uebel (Ger. P. 210803) performs the concentration in stages. First he distils the dilute nitric acid at higher temperatures with sulphuric acid of medium concentration, and treats the distillate with stronger sulphuric acid at lower temperatures; the sulphuric acid used in the second stage is afterwards employed for the first; it is employed at a strength of 80 per cent., to the extent of three times the quantity of the nitric acid. From the second still the nitric acid comes out with 70 to 75 per cent. HNO_3; it runs into the first still, and here a vapour of 90 per cent. comes out, which by partial cooling can be made to yield acid of 95 to 98 per cent. HNO_3. In this way also the waste acid mixtures from nitrating processes may be utilised.

Vietinghoff-Scheel (Ger. P. appl. V8284; later on withdrawn) concentrates the acid by first converting it into ammonium nitrate, drying this, and distilling it with concentrated sulphuric acid.

Plath (B. P. 9133 of 1901) makes clear concentrated nitric acid by interposing between the perpendicular cooling-pipes and the receiving-vessel a cooling-worm about 80 ft. long, air being passed through opposite to the current of acid, and the temperature in the cooling-tub being regulated in such a manner that the acid comes out both cold and free from lower nitrogen oxides.

Brauer (Ger. P. 222680; U.S. P. 1008690; B. P. 14381 of 1910) concentrates nitric acid by heating with phosphoric or arsenic acid. These acids have the advantage that they do not, like sulphuric acid, form a chemical combination with nitric acid; hence the heating need not be driven higher than the boiling-point of the nitric acid, which means a saving of fuel and the avoiding of losses by the splitting off of lower nitrogen oxides.

The Swedish Nitric Syndicate (B. P. 10392 of 1908; Ger. Ps. 233031 and 236341; Fr. Ps. 402078 and 402079; U.S. Ps. of Sohlmann, 1009196 and 1009197) concentrate weak nitric acid, especially that obtained by the oxidation of atmospheric nitrogen, by distilling with sulphuric acid in a continuous manner, the acids flowing down in a column heated externally, while a current of hot air (of which but little is required) passes upwards in the column. Or else the concentration is effected in two steps: (1) to about 60 per cent. by direct contact with the gases from the electric furnaces; (2) to 90 to 97 per cent. by distilling with strong sulphuric acid, as above described. The waste heat from the furnace gases is utilised in various ways.

Pauling (B. P. 22037 of 1909) heats dilute nitric acid to a temperature at which it is decomposed into a mixture of NO_2, O, and

H_2O, and rapidly cools the products. Thus a mixture of NO_2 and O, nearly free from water, is obtained, from which concentrated nitric acid is readily prepared. His B. P. 22320 of 1910 describes the concentration of nitric acid by causing it to trickle down in a vertical column, together with sulphuric acid, in an ascending stream of steam or hot gases. B. P. 22322 of 1910 describes a modification of this process. His U.S. P. 993868 describes dehydrating nitric acid vapours by passing against a counter-current of sulphuric acid, kept at a temperature near that of the vapours at all stages of the process. He has also obtained U.S. Ps. 993868, 1031864, 1031865, 1074287, 1079541; Aust. Ps. 48815, 48816; Fr. Ps. 450448, 463859. The newest forms of his system are described in Ger. Ps. 257809 and 274165. According to these, it is best to employ nitric acid as free as possible from organic substances, nitrogen oxides, and nitrosulphuric acid. From a mixture of 1 part of 48 per cent. nitric acid and 2 parts of 94 per cent. sulphuric acid it is easy to obtain nitric acid of 96 to 98 per cent., without any weaker acid coming behind. It is best to charge the mixture on the top of a vertical tube, filled with the dividing bodies, and to introduce from below dried, but not superheated steam, or inert gas containing very much aqueous vapour. According to his Fr. P. 463859 (transferred to the Norsk Hydro-Elektrisk Kvaelstofaktieselskab), nitric acid of 30 per cent. is gradually passed through a series of evaporators, whereby acids of 40, 50, 60, 68 per cent. are obtained. The vapours are passed through dephlegmators, from which the acid goes back to the evaporators. The vapours are introduced into the dephlegmators at various heights; the acid to be concentrated also goes into a dephlegmator, a little below the entrance of acid of 15 to 20 per cent. If part of the concentrated nitric acid is added to the mixture of sulphuric acid and dilute nitric acid, it is possible to obtain any desired concentration of nitric acid, even by 88 per cent. sulphuric acid.

Dieffenbach and Uebel (Ger. P. 238370) concentrate nitric acid by distilling it over pyro- or metaphosphoric or the analogous arsenic acids, or acid salts of these, in vessels made of quartz. *E.g.*, on heating aqueous nitric acid with pyrophosphoric acid at 110° to 115°, nitric acid of 99 per cent. distils over. The orthophosphoric acid remaining behind is reconverted into pyrophosphoric acid by heating to about 210°.

Hale and Scott (B. Ps. 24379 and 25386 of 1910) cause dilute nitric acid to be absorbed in kieselguhr and heat this in an earthenware or cast-iron retort, if necessary provided with a stirring arrangement, under reduced pressure. The vapours are condensed, and acid of any desired strength may be produced by adjusting the temperature of distillation and the degree of vacuum.

The Farbwerke Höchst (Fr. P. 432990) concentrate nitric acid of 60 or 62 per cent. to a higher point by passing a mixture of nitrogen peroxide and oxygen through it. For this process they have also obtained the B. Ps. 15948, 1911; 13842, 1913; Ger. P. 249328; Aust. P. 55242; U.S. P. 1050160 (taken out by Moest and Berneck). They obtain concentrated nitric acid by treating nitric acid of 60 to 62 per cent. with liquid or gaseous nitrogen peroxide, and then with oxygen, on the counter-current system. The oxygen enters at one end of the apparatus, the N_2O_4 at an intermediate point. Preferably it is obtained by passing a current of oxygen through liquid N_2O_4. The oxygen is employed in slight excess; according to their Ger. P. 249329, they employ oxygen in the compressed state, and reintroduce any oxygen and nitric oxide gases, escaping at the bottom, into the system.

A new patent of that firm (B. P. 4345 of 1915, taken out by O. Imray; U.S. P. 1180061, and Swed. P. 40600, of Moest) states that if nitric acid is intimately mixed with a larger proportion of liquid nitrogen peroxide than corresponds to the maximum of solubility, two separate layers are formed, both of them consisting of nitric acid and NO_2, but one of them—mostly that of lower specific gravity—contains a more concentrated acid, up to 100 per cent. The other layer contains a more diluted acid than that which has been at first used. Thus it is possible to obtain highly concentrated nitric acid by means of liquid NO_2. The NO_2 is eliminated by distillation from the layer containing the more concentrated acid. The other layer, containing dilute nitric acid and NO_2, may be enriched, for instance, by treating it with oxygen, and further concentrated by the new process. In order to avoid loss of NO_2, a reflux apparatus is employed. The process may be operated under pressure; it is advantageous to agitate well.

The *Soc. anon. le Nitrogène* (Aust. P. appl. A133; Fr. P. 424598) produce nitric acid upwards of 95 per cent. HNO_3 by treating a mixture of liquid nitrogen peroxide, water, and oxygen in molecular proportions under high pressure.

The Salpetersäure-Industrie-Gesellschaft, Gelsenkirchen (Ger. P. 180052), concentrate nitric acid up to 100 per cent. by electrolysis. The nitrogen oxides formed thereby at the cathode are introduced at the anode and there oxidised by the oxygen formed into HNO_3, after having been liquefied by cooling. Their Ger. P. 180587 describes the employment of waste acid from nitrating processes as anodic liquor in the above process. Another modification is described in their Ger. P. 184958.

Imray (B. P. 15948 of 1911) dissolves in ordinary nitric acid of 60 to 62 per cent. gaseous or liquid nitrogen peroxide, and treats the mixture with oxygen, whereby the peroxide is oxidised into nitric acid and concentrated nitric acid is obtained. The same process is described in the Ger. P. 249328 of the Salpetersäure-Industrie-Gesellschaft.

The Farbwerke Höchst have obtained for the same process the B. P. 15948 of 1911; Ger. P. 249328 and Aust. P. appl. 7082. According to their Ger. P. 249329 the oxygen is employed in the compressed state, and the escaping oxygen and nitric oxide gases are reintroduced into the process.

Schlarb (Ger. P. 243840) obtains concentrated nitric acid from any description of nitrous gases by treating them with water in the presence of the oxides or basic nitrates of iron, aluminium, or chromium, driving off the nitric acid from the nitrate liquors obtained (if necessary, after concentrating them in vacuo) by heating, continually under diminished pressure. Thus marketable nitric acid of 40° Bé. and more, as clear as water, is obtained; the basic nitrates or hydroxides remaining behind are used over again for the absorbing process.

Friderich (B. P. 319 of 1911) treats a molecular mixture of liquid nitrogen peroxide and water with oxygen. According to his B. P. 493 of 1911, in lieu of liquid nitrogen peroxide, the product of absorbing N_2O_4 by wood charcoal, etc., may be used.

According to Hall's B. P. 11245 of 1911, the material is placed on a grate within a tower, which is heated on the outside; a current of hot air, dried by sulphuric acid, is passed in from the top downwards, or *vice versa*. His B. P. 21724 of 1911 prescribes intimately mixing the mixture of kieselguhr and nitric acid with sulphuric acid, which promotes the conveyance of heat into the interior of the mass during distillation and retains any water present or newly formed. After distilling off the nitric acid, both the sulphuric acid and the kieselguhr can be recovered by treating with water; the sulphuric acid must, of course, be reconcentrated. According to his B. P. 19965 of 1911, the distillation is carried out in a retort with inclined bottom, and an outlet through which the dry kieselguhr can easily pass. By means of perpendicular, horizontal, or serpentine rods or pipes, the heat is transferred from the outside to the interior. An outside jacket allows the gases to gyrate round the retort.

Collett (B. Ps. 7597 and 22746, 1913; Fr. Ps. 357221, 447106, 450448; Aust. P. 62169; U.S. Ps. 854928, 1079541, 1133840, 1154289, 1158181, 1184926; Can. Ps. 157489 and 157490).

From a mixture of sulphuric and nitric acid the latter is distilled off; the vapours are carried over sulphuric acid, in order to give up the water, and are then condensed. The nitric-acid vapours are carried through several towers in which sulphuric acid is run down; that acid is cooled between each two towers. The evaporation of the nitric acid is carried out in several communicating vessels, and the vapours are passed into a dephlegmating apparatus at various heights; from this apparatus continuously acid containing 15 to 20 per cent. HNO_3 is run off.

Sohlmann and Lundholm (U.S. P. 1009197) concentrate nitric acid (made from atmospheric nitrogen) by hot gases, which are used in succession for concentrating dilute sulphuric acid, distilling strong nitric acid from its mixture with sulphuric acid, and ultimately for the concentration of dilute nitric acid by direct contact.

Moscicki (Ger. P. 230170) places between a furnace, in which vapours of nitric acid are made from air, and the absorbing-apparatus a tower containing suitable packing, in which a mixture of sulphuric acid of 60° to 61° Bé. and nitric acid of 60 per cent. is run down. The furnace gases take up nitric acid from this mixture and then pass into another tower; on their way they cool down and allow most of the nitric acid to separate in a concentrated form. The non-condensed remainder of nitric acid is retained in the second tower and by other suitable apparatus. His Austrian patent is No. 38937. A plant for carrying out this process has been erected by the Aluminium-Industrie Akt. Ges. at Chippy, near Siders (Valais).

According to Fr. P. 472775 of the Farbwerke Höchst, and U.S. P. 1145162 (taken out by Moest and Eckardt), nitric acid is concentrated in a retort, provided with a dephlegmating column, heated to a suitable temperature by means of a coating or by the nitric vapours themselves. The acid to be concentrated is continuously run into the column, and the strong acid continuously run out at the bottom.

Raschig (B. P. 3208, 1915; Ger. P. 286973; U.S. Ps. 1130104, 1163174) combines two apparatus for the concentration of nitric acid, both of them consisting of shallow, flat-bottomed pans, made of cast-iron, lined with lead, with ribs compelling the liquid to travel a long way. In the first of these pans vapours of concentrated nitric acid are evolved from dilute nitric acid of 50 per cent. and strong sulphuric acid (92 per cent.), the mixture being heated to about

150° by means of steam of 10 to 12 atmospheres' pressure, circulating in a worm cast in the pan-bottom. On its way through the pan nearly all the nitric acid is evaporated; it is condensed in a stoneware worm, cooled outside, and runs off as highly concentrated nitric acid. The dilute sulphuric acid coming out of this pan is forced by air-pressure into a second pan, placed 20 ft. above the first, working under a vacuum, and likewise heated to 150° by indirect steam. In this pan the dilute sulphuric acid gives off water, and the remainder of the nitric acid in the state of vapour. Both of them are condensed in a stoneware worm, the highly diluted nitric acid running off freely by a descending pipe, 33 ft. long, and a dipping-pot. This dilute nitric acid is employed in towers for absorbing nitrous vapours, and thus again brought to a concentration of 50 per cent. HNO_3. The concentrated sulphuric acid runs out of the second pan through a long descending pipe, in which it is automatically kept by the atmospheric pressure at such a height that it feeds the lower pan.

In Ger. Ps. 286122 and 292622, Raschig describes a cylindrical packing for absorbing and reaction towers.

Rossi (Fr. P. 455531) brings nitric acid into contact with hot air, with or without steam, in such a manner that the temperature of the gases on leaving the apparatus is below 100°. According to his Fr. P. 455532, a mixture of dilute nitric acid with one and a half times its weight of concentrated sulphuric acid is passed on in the contrary direction to a current of air and steam, by which process very pure nitric acid, up to 99.8 per cent., is obtained. According to his Fr. P. 463830, nitric acid is concentrated up to 42° Bé. in a vacuum apparatus, allowing of dephlegmation and fractionation.

The Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. Ps. 27239, 1913; 19792, 1914; Ger. Ps. 278367 and 289745; Fr. Ps. 465504 and 474995) pass the vapours of dilute nitric acid through a tower fed with concentrated sulphuric acid, from which practically dry vapours of nitric acid escape. Part of the sulphuric acid is run out of the tower at the bottom, cooled, and reintroduced higher up. The dilute sulphuric acid formed is before its reconcentration passed through an apparatus in which the nitric acid contained in it is driven out by a current of air; the vapours are passed through the first tower. According to their Ger. P. 292385 the liquid is evaporated by indirect heating. The central part of the tower is kept at the low temperature required for the drying operation, by drawing off part of the running-down acid cooling it, and reintroducing it into the tower at a higher point.

Titlestad (U.S. P. 1178888) makes a mixture of vaporised and liquid nitric acid meet a counter-current of concentrated sulphuric acid.

Schall and the Stickstoffwerke Akt. Ges. at Herringen (Ger. P. 280965) pass a mixture of dilute nitric acid and a drying-agent through a tower, provided with a central tube through which heating-gases flow, and which on the outside has ribs in the form of spirals or steps, so that the mixture flows over it evenly on a long way. This tube is conveniently made of an alloy of iron with silicon or chromium.

The Salpetersäure-Industrie Gesellschaft, according to B. P. 18113, 1913; Aust. P. 61387, concentrates nitric acid by mixing it with sulphuric acid or another drying-agent by means of steam or a mixture of steam and gases, carrying back part of the distilling concentrated nitric acid into the mixture, which makes it possible to employ less highly concentrated sulphuric acid. This process is specially adapted for utilising the waste acid from the manufacture of nitroglycerin.

Manufacture of Nitric Monohydrate (nitric acid of 100 per cent.).—The Verein chemischer Fabriken at Mannheim (B. P. 20189, 1912; Ger. P. 281211; Fr. P. 462290; U.S. P. 1115192, taken out by Hausmann) employs for this purpose a still of the form of a flat dish, heated merely at the bottom, the top being cooled by air or cold gases. Thereby any vapours of sulphuric acid are kept back, and the nitric acid is obtained free from sulphuric acid. The depth of liquid in the still is only 20 to 30 mm., and the liquid is compelled by concentric partitions to flow in a long course over the heated bottom, so that the mixed acids can be continuously run in and the sulphuric acid can be continuously run out. The nitric acid vapours are carried away by air passing over the liquid, and are condensed in worms, tourills, and towers, which is much more easily done than in vacuum apparatus. This apparatus, when comparing the total heating surfaces, does five or six times the work of a vacuum plant; besides most highly concentrated and monohydrated nitric acid, it produces only slight quantities of weaker acid, quite free from nitrogen peroxide.

Hof (Ger. P. 279131; U.S. P. 1099368) employs for the continuous distillation and concentration of acids an inclined tube, made of quartz glass, zirconium glass, or other acid-proof materials.

Bayerische Akt.-Ges. f. Chem. und Landwirtschaftl. Fabrikate, H. Hackl, and H. Bunzel (Ger. P. 307601, 9th March 1916). Barium nitrate is heated with sulphuric acid in a vessel through which the mixture is conveyed by a screw device in order to allow of a continuous process.

H. Frischer (B. P. 137834, 12th January 1920, conv. 31st August 1916). Dilute nitric acid is vaporised by introducing it into a liquid of high boiling-point, which is unaffected by it, such as phosphoric acid, sulphuric acid, or arsenic acid, the liquid being heated to a high temperature (140° to 160° C.) and the nitric vapours conducted to a dephlegmator. Instead of causing the dilute nitric acid to pass direct into the vaporising apparatus, it may first be introduced into the dephlegmator, from which a part is drawn off as concentrated acid, and the remainder then vaporised by the heating liquid.

Leitch (B. P. 125616, 12th September 1916). Highly concentrated nitric acid such as 91 per cent. acid is prepared by distilling $NaNO_3$ or dilute HNO_3 with relatively weak sulphuric acid such as B.O.V. of 84 per cent. strength, and passing the vapours through a fractionating column or other dephlegmator so that water or the weaker acid flows back to the still. The temperature of the column may be regulated, as by a steam jacket or by the heat of the vapours of the still, so regulating the strength of the distillate. The operation may be effected under reduced pressure.

Reinau (Ger. P. 305171, 30th September 1916). $NaNO_3$ and $NaHSO_4$ are brought into reaction, and the resulting Na_2SO_4 is returned to process for converting dilute nitric acid to solid $NaNO_3$ and $NaHSO_4$ (see Nos. 299001 and 299007).

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Jap. 30228, 25th October 1916). Nitrosulphuric acid is first made by absorption in sulphuric acid. By treating the nitrosulphuric acid with steam mixed with nitric acid vapour, concentrated nitric acid can be obtained on the one hand and strong nitrous acid gas on the other hand, and from the latter dilute nitric acid is regenerated and serves for the treatment with nitrosulphuric acid.

Washburn (Can. P. 173157, 14th November 1916). A mixture of gases containing NH_3 and O is subjected to a suitable catalyser at such a velocity as to cause an oxide of nitrogen and free NH_3 to appear in the products of reaction. The products are then concentrated and separated.

Washburn (Can. P. 173158, 14th November 1916). The NH_4NO_3 from the concentrated products specified in the preceding patent is treated with H_2SO_4 to give concentrated nitric acid and to form $(NH_4)_2SO_4$.

Farbw. vorm Meister Lucius und Brüning (Swed. P. 41751, 27th December 1916). Dilute nitric acid of concentration greater than that of an acid of lowest vapour pressure (about 68 per cent.) is heated and the vapours are allowed to pass through a separating column kept at a temperature corresponding to the desired concentration.

Maxted and Smith (B. P. 126704, 19th February 1917). In absorption of oxides of nitrogen a large excess of NO_2 is used (to effect displacement of equilibrium of the reaction towards concentrated nitric acid) and the excess is afterwards removed by distillation. By employing five and seven times the theoretical quantity of NO_2 required by the water present, nitric acid of 90 and 94.5 per cent. concentration, respectively, is obtained.

Pauling (Ger. P. 305553, 31st May 1917). The aqueous nitric acid and the dehydrating agent with which it is mixed, *e.g.*, sulphuric acid, are heated, before or after mixing, and the heated mixture is submitted to the action of a current of dry air or other inert gas, also heated if necessary; the evolved nitric acid vapours may be further treated with sulphuric acid.

Badische Anilin- und Sodafabrik (Ger. P. 302411, 24th July 1917). A mixture of dilute nitric acid and concentrated sulphuric acid passes down two separate columns in which it is treated with a counter-current of steam. Concentrated nitric acid is delivered from the first column, and a portion of the vapour issuing from the second column, in which the last traces of nitric acid are removed from the mixture, is employed in the first column instead of fresh steam.

Birkeland, Assignor to Norsk Hydro-Elektrisk Kvaelstofaktieselskab (U.S. P. 1236662, 14th August 1917). A metal capable of forming a nitrate is treated with dilute nitric acid and the solution of the nitrate evaporated. The salt is decomposed with steam to metal oxide and a gas containing oxides of nitrogen, the peroxide being converted to nitric oxide by steam and oxygen.

Zeisberg (Can. P. 178118, 4th September 1917). A mixture of nitric and sulphuric acids is caused to run down a column containing pumice stone to meet the vapours from boiling sulphuric acid of any convenient strength. The vapours condense and the heat given up drives out the nitric acid which is condensed and collected. The small amounts of the lower oxides of nitrogen are absorbed in water.

Brooke (B. P. 120951, 8th November 1917). Waste acids containing nitric acid such as are produced in making picric acid, are concentrated in earthenware, enamelled, or other acid-proof vessels provided with coils or jackets through which pressure or superheated steam is circulated. A battery of vessels each fed from a pipe and discharging into a trough may be used, the vapours being led to a fume pipe. Alternatively, the vessels may be arranged so that the acid flows through them in series.

Toniolo (B. P. 121635, 27th December 1917). In the manufacture of nitric acid by absorbing nitrogen oxides in water in a series of towers in counter-current, strong cooling of the acid passing from tower to tower is effected by artificial refrigeration so that the acid entering each tower may be in the neighbourhood of its freezing-point, *e.g.*, the acid entering the last tower may be at 4° to 5° C., that entering a preceding tower receiving 13° acid at − 8° C. and in an earlier tower receiving 65 per cent. acid at − 25° C.

Cocking and Kynoch (B. P. 130038, 2nd January 1918). Dilute nitric acid is neutralised with ammonia, the resulting solution evaporated to crystallisation of ammonium nitrate, and the dried salt decomposed at reduced pressure with strong sulphuric acid (preferably waste acid from nitrating plant).

General Chemical Company (B. P. 120546, 28th February 1918). Dilute nitric acid is concentrated by means of air and sulphuric acid in a distilling apparatus. A suitable construction, with operation, is specified.

General Chemical Company (B. P. 124759, 28th February 1918). Dilute nitric acid from absorption is fed to a concentrating apparatus, having two trays containing divisions from which liquid may overflow into other divisions, and having provision for allowing overflow into a tower. Hot concentrated sulphuric acid is fed in and air, preferably hot. Nitric acid vapour escapes, and on condensation yields an acid of 97 per cent. Dilute sulphuric acid is withdrawn.

Guye (B. P. 131335, 2nd May 1918). Aqueous nitric acid is concentrated by passing into it a current of ozonised oxygen or air and nitrogen peroxide, which interact to form nitric anhydride, the latter combining with the water present in the nitric acid.

Gros and Bouchardy (B. P. 131336, 2nd May 1918). In the manufacture of nitric acid of about 98 to 100 per cent. from liquid NO_2, O, and H_2O, or dilute nitric acid, the NO_2 is employed in such excess as to maintain the liquid saturated throughout the operation, that is, the ratio of NO_2 to H_2O is at least 15 : 1. The action of the O is continued until the lower layer consists of HNO_3 of 98 to 100 per cent. strength containing NO_2, and the upper, of NO_2 containing a little HNO_3 of the same strength. The O may be employed under pressure, *e.g.*, 20 atmospheres and a somewhat raised temperature, not above 30° C., may be used. The mixture is agitated during the reaction. The operation may be effected intermittently or continuously. In the former case, the two layers which form may be separated and the HNO_3 layer may be distilled to recover the excess of NO_2, while the other layer which is mostly NO_2 may be used again; or the whole mixture may be distilled together.

Marks (B. P. 135535, 6th September 1918). Concentrated nitric acid is produced from mixtures of nitric and sulphuric acids, such as the waste acids obtained in nitrating cellulose, containing 3 to 25 per cent. HNO_3 and not less than 64 per cent. H_2SO_4, by distributing the acids uniformly over pieces of quartz or other material of 2 to 3 in. in a tower at the lower end of which steam or a hot gas is admitted, the temperature of the vapours leaving the upper end of the tower being kept below 215° F., and preferably at or below 205° F. The vapours are passed to a condenser, and the uncondensed gases are absorbed in water and returned to the tower. The condensate is 90 to 99.7 per cent. HNO_3. The distributor for the acids entering the tower is formed with liquid discharging openings and with openings through which vapours from the tower pass a coupling leading to the condenser. The acids are admitted to the distributor by a pipe. The absorbed gases are returned by a pipe.

Bayer and Co. (Ger. P. 310081, 7th September 1918). The required heat for the process is secured by employing strongly preheated H_2SO_4 and utilising the heat liberated by mixing dilute nitric acid with the sulphuric acid. The nitric acid is driven off in a column apparatus which is charged with filling material and provided at the top with a vessel into which dilute nitric acid and hot concentrated sulphuric acid flow together. The temperature of the sulphuric acid flowing in is maintained so high that the temperature of the acid leaving the column is at least 100° C. Into the bottom of the column air is blown in amount just sufficient completely to denitrate the acid flowing from the column. The sulphuric acid employed is so concentrated and the amount of 40 to 50 per cent. nitric acid added is such that the sulphuric acid leaving the apparatus has a strength of 74 per cent. In this manner a nitric acid of about 99.5 per cent. strength is obtained with a minimum amount of air and without the use of steam.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. P. 120378, 19th September 1918). The production of concentrated nitric acid from NO_2 or other oxides of nitrogen is effected by passing the gas together with O and H_2O or dilute nitric acid under pressure through a series of reaction vessels, so arranged that the current of O passes in the same direction as the liquid through each individual reaction vessel, while the O and liquid pass in opposite directions through the apparatus as a whole. The process may be carried out at a pressure of 10 atmospheres and a temperature of 70° C. Apparatus for use in carrying the process into effect is described.

Zeisberg (B. P. 135535, 6th September 1918; U S. P. 1292948, 28th January 1919). Acid mixtures containing 64 per cent. or more of H_2SO_4 and from 3 to 25 per cent. HNO_3 such as spent acids from nitrating cellulose, are treated with a current of hot gases and steam and the nitric acid vapours are carried away and condensed. A concentrating tower for carrying out this process is illustrated and described.

Davis (U.S. P. 1314485, 26th August 1919). Dilute nitric acid is pre-heated and allowed to flow down a suitably packed tower, at the base of which are introduced nitrous gases at a temperature above 300° C.

Hechenbleikner (U.S. P. 1314802, 2nd September 1919). The apparatus comprises a series of absorption towers arranged in a row with reservoirs at their lower ends having overflow outlets successively from one to another in the row. Pumps and piping are arranged so that liquid from each reservoir can be pumped to the top of its own tower for recirculation. The gases flow through the towers in the same direction as the liquid.

Thomas (U.S. P. 1283598, 5th November 1919). Concentrated nitric acid is obtained by absorbing nitrogenous gases such as those generated from air in an electric furnace in a liquid such as water under pressure, and at the same time converting the lower oxides of nitrogen into nitric acid by electrolysis, at a temperature below 40° C.

Jensen (U.S. P. 1324255, 9th December 1919). Nitric acid containing oxides of nitrogen is passed in counter-current to nitric acid vapours so that N_2O_4 is expelled and condensed. The acid purified by this treatment is distilled and dephlegmated, producing dilute liquid acid and vapours of highly concentrated acid and a portion of the latter is passed in counter-current with the acid to be purified. Another portion is condensed to produce highly concentrated acid.

Frischer (B. P. 137831, 12th January 1920). Liquids are evaporated by being mixed with a heated liquid having a boiling point higher than that of the liquid to be treated, the two liquids having no chemical action on each other. The process is especially described in connection with concentrating nitric acid, suitable heating liquids being sulphuric acid, phosphoric acid, or solutions of appropriate salts, or materials in a molten state. The vapour thus produced is led into a dephlegmator, and a portion of the vapour leaving the dephlegmator may be returned thereto along with the freshly vaporised acid in order that a greater degree of concentration may be attained.

Bergve and Jensen (U.S. P. 1338417, 27th April 1920; Can. P. 201480, 29th June 1920). Concentrated nitric acid is continuously produced by subjecting nitrogen peroxide under pressure to the action of oxygen in two or more scrubbers supplied with water or dilute nitric acid. The oxygen is retained in contact with the liquid as long as possible, and for this purpose the oxygen and liquid are passed through the apparatus in the same direction in the sections of the plant where the reactions take place. The nitrogen oxides are employed in gaseous state and a temperature of 70° C., which is favourable for the reactions, may be maintained by the heat produced by the oxidation of the nitrogen oxides so that external heating is not necessary. The oxygen is completely utilised and the residual gas includes only the small quantities of impurities present in the gases used. An apparatus is described.

Bohre (U.S. P. 1338418, 27th April 1920; Can. P. 201482, 29th June 1920). Hot nitrous gases are brought in contact with nitric acid or sulphuric acid to be concentrated, the resulting vapours are condensed by contact with a cooling liquid, and the cooling liquid is then cooled for condensing further quantities of the vapours by passing a gas through it.

Guye (B. P. 131335, 1918; U.S. P. 1348873, 10th August 1920). Liquid nitrogen peroxide is caused to react for a prolonged time with water or dilute nitric acid in an atmosphere of oxygen. To keep the water saturated, the proportion of nitrogen peroxide to water must be at least 15 : 1. Two immiscible layers are formed, of which one, representing about four-fifths of the volume, contains nitric acid (98 to 100 per cent. HNO_3) and its own weight of nitrogen peroxide. The other consists of nitrogen peroxide containing 2 to 5 per cent. HNO_3. The nitric acid layer is easily separated by decantation and then distilled, or it may be recovered by distillation of the mixture under reduced pressure. The time of reaction may be reduced by agitation, by increasing the temperature to 30° C., or by compressing the oxygen up to 20 atmospheres. An increase of 1 to 10 atmospheres reduces the time from thirty-one to four hours. The process may be intermittent or continuous.

Moest and Eckhardt (Can. P. 206819, 21st December 1920). Nitric acid, the percentage strength of which is higher than that of the acid of lowest vapour pressure, is heated without additional substances, the vapours are passed through a fractionating column in which the temperature is kept at a degree corresponding with the desired concentration, and the vapours passing over are condensed.

Jensen (Can. P. 207546, 11th January 1921). Nitric acid to be concentrated is partially evaporated while maintaining the acid in motion and causing the separation of precipitated solid, and the vapours are passed into contact with concentrated sulphuric acid.

Utilisation of Nitre Cake.

Claes (B. P. 1072 of 1900) describes the manufacture of "polysulphates" from nitre cake and sulphuric acid as a commercial article.

Kirkman (B. P. 5703 of 1889) employs it as an absorbent for ammonia, in which case a profitable utilisation of Na_2SO_4 will be very difficult.

Giles, Roberts, and Boake (B. P. 11979 of 1890) convert ordinary nitre cake by addition of sulphuric acid into "penta-sulphate," $Na_2O, 5SO_3, 3H_2O$, which can be packed in iron drums [?] or ordinary casks and usefully employed for certain purposes (*cf.* Uebel's "polysulphate," p. 149).

Barbier (U.S. P. 484546) dissolves nitre cake to form a solution of 35° to 45° Baumé, and cools this down to about 10° C., by which process it is decomposed into crystallised sodium sulphate and free sulphuric acid [?].

Cheeseman (U.S. P. 714145) describes a process which neutralises a solution of nitre cake by lime (or calcium carbonate), separates the calcium sulphate by filtration or otherwise, runs off the solution of sodium sulphate and utilises this, for instance, for the manufacture of "blanc fix" (pearl hardening), by precipitation with barium hydrosulphide solution.

Bollé (B. P. 6898 of 1904) mixes the bisulphate with about 12 per cent. of wood shavings and about 2 per cent. of coke in a retort provided with a mechanical agitator, and then heats the mixture with agitation, till all the SO_2 formed has been driven out and only neutral sulphate remains. (This is a communication from the Chemische Fabrik Grunau.)

Nibelius (U.S. P. 873070) treats nitre cake with a volatile liquid which dissolves the acid, but not the sulphate, removes the latter, and distils the solution under diminished pressure to recover the volatile solvent, sulphuric acid remaining behind.

Parker (B. P. 24639 of 1903) brings a solution of nitre cake into contact with a large excess of iron, thus forming ferrous sulphate and (by reduction of any nitrate present) ammonia. This solution is worked up for ferrous salt, ammonia, and sodium sulphate.

G. E. Davis (B. P. 14749 of 1903) adds to a hot concentrated solution of nitre cake, clay, or bauxite, and heats and agitates by high-pressure steam. On cooling, a mass is obtained, suitable for sewage precipitation, etc.; but it is usually worked up by dissolving, crystallising out the excess of sodium sulphate, and then working for sodium alum.

The Soc. Dior fils (Fr. P. 417816) makes sulphuric acid from alkaline sulphates or bisulphates, to which is added bauxite or aluminium sulphate, by heating in a muffle, so as to liberate SO_2 and SO_3, which are then transformed into pure concentrated sulphuric acid. The aluminium sulphate, etc., is extracted from the residue with water and is treated with CO_2, to obtain an alkaline carbonate. An addition to this patent provides for the addition of coke-dust to the above-described mixture; this mixture is heated to 1100° to 1250° in a muffle furnace. When the mixture begins to lose its black colour and white specks appear, it is withdrawn from the furnace and treated as above.

Zahn (Fr. P. 389898; U.S. P. 921329) adds to sodium bisulphate just sufficient water to form hydrated sulphuric acid and the normal sulphate; say 6 or 7 kil. water to 100 bisulphate. Part of the sulphuric acid escapes on heating, while the mixture becomes pasty, and in this state it is introduced into a muffle and calcined.

Prud'homme (Fr. P. 400030) obtains SO_3, or a mixture of SO_2 and O, by heating natural or artificial sulphates in an electric furnace with simultaneous formation of anhydrous bases. By adding SiO_2, or Al_2O_3, or Fe_2O_3 to the sulphates, the decomposition of the latter is rendered more complete.

Uebel (Ger. P. 226110) exposes bisulphate in a finely divided state to the action of superheated air, or steam, or fire gases, in a tower, the bottom of which consists of a calcining-hearth.

Benker (B. P. 1844 of 1907; Ger. Ps. 204354 and 204703; U.S. P. 899284; Fr. P. 381863) mixes nitre cake with fine sand, or finely divided silicates, or anhydrous sulphates of Na, K, or Ca, in such proportions that the mass does not fuse on heating. Sulphuric acid may be distilled off and anhydrous Na_2SO_4 remains behind, without the destruction of the apparatus which takes place when the bisulphate by itself is strongly heated. His Ger. P. 204703 gives the following instructions. One hundred parts neutral sodium sulphate and 25 parts nitre cake, both in the state of powder, are introduced into a heated muffle furnace, where the mixture at once gives off sulphuric acid without getting into the fused state. When the development of acid ceases, again 25 parts nitre cake are added, but without any more neutral sodium sulphate, and this proceeding is continued, until altogether 100 parts nitre cake have been put in upon 100 parts neutral sulphate. Now half of the charge is drawn out of the furnace, and the remaining half is spread out, so that more nitre cake can be put in, and so forth, without ever having to put in any more neutral sulphate. The sulphuric acid vapours pass first through a cooler, where acid of 55° Bé. is condensed, amounting to about one-half of the total acid present. The vapours coming away from the cooler, consisting of H_2SO_4, SO_3, and steam, are taken through a coke filter, where by means of a little steam, acid of 40° to 50° Bé. is condensed. If it were intended to produce anhydrous SO_3, a special condensing plant would have to be employed for the condensation of hydrated acid, and another such plant for condensing the SO_3 in the last stage of the process.

Campbell and Walker (B. P. 9782 of 1894) grind nitre cake with nitrate of soda and charge the mixture into retorts provided with a mechanical agitator.

Garroway (B. P. 6777 of 1899) mixes ordinary acid nitre cake with sodium nitrate, heats the mixture in a retort, and blows a spray of weak nitric acid by means of compressed air over the mixture. The nitrogen oxides, mixed with steam and air, are regenerated by condensing-tubes and towers into nitric acid. It is alleged that ultimately a 96 per cent. acid can be produced. The residue is neutral saltcake, testing 98.36 per cent.

The Aktiengesellschaft Dynamit Nobel at Vienna (Ger. P. 263120) describes the production of nitre cake in a form allowing of immediate calcination, for the purpose of making neutral sulphate, without the necessity of producing hydrochloric acid at the same time. This cannot be done by heating the nitre cake by itself, because on the large scale this is impossible without fusing it, which destroys every known description of apparatus. Nor can this be prevented by mixing the nitre cake with silica, silicates, anhydrous sulphates of sodium, potassium, calcium, etc., as proposed by Benker. But it is possible by heating the nitre cake with coal, as prescribed in the Ger. P. 63189 of Rommenhöller and Luhmann, or with sawdust (B. P. 6898, 1904). According to the new process (Ger. P. 263120), a carbonisable substance, like sawdust, peat, etc., is put into the liquid hot bisulphate as it is run out of the nitric-acid still; this causes a tempestuous evolution of gas, and the bisulphate solidifies as a loose, spongy, extremely porous mass. On calcining this in a muffle, the coal formed thereby acts as a reducing agent and goes away as CO_2, whilst the bisulphate turns even more porous and therefore less fusible, and can therefore be calcined at the normal temperature of a saltcake furnace. For this purpose from 2 to 10 per cent. sawdust is stirred into the hot bisulphate run out of the nitric-acid stills, and the mixture is allowed to solidify on a cooling place, forming a black, spongy mass which on calcination is converted into a white mass without fusion, and forms neutral sulphate of normal composition.

Löffler (U.S. P. 1104911) describes the same process.

Stanes and Rogé (B. P. of Hunnybun, No. 18605, 1914) heat the acid sulphate with sulphur in a muffle, collect the liberated sulphur dioxide, and convert the residual anhydrous sulphite into bisulphite by treatment with sulphuric acid.

Mackenzie (B. P. 13907, 1915; Ger. P. 291775) melts nitre cake in a saltcake-pot; after driving off the moisture and the weak acid, the charge is pushed on to the roaster, where the sulphuric acid is driven out and led into a Glover tower or other suitable apparatus.

Haas[1] uses nitre cake as a partial substitute for aluminium sulphate in the sizing of paper.

Howard (U.S. P. 1193552) mixes the $NaHSO_4$ with an excess of NaCl and sufficient sulphuric acid to produce normal Na_2SO_4, and heats the mixture in the hydrochloric-acid furnace.

The Metallbank und Metallurgische Gesellschaft und Hans Klencke (Ger. P. 274873) obtain by heating the nitre cake in a continuous way neutral saltcake and concentrated sulphuric acid, in a single furnace space, the neutral saltcake formed being liquefied. Their apparatus is a trough of highly acid-resisting cast iron, consisting of several pieces, and resting on a fireclay bed. It is provided with a cover of fireclay, volvic lava, or similar matters, or of cast iron with an insulating layer for keeping it hot. The fire gases enter at one end, perpendicularly to the bath, and leave the apparatus at the other end. The flame should be clear, and not smoky. The nitre cake is introduced mechanically and continuously by an opening lined with "neutral iron"; the neutral sulphate is removed at the opposite end by several outlets at different heights. In order to protect the cast-iron trough against the destructive action of the liquid bisulphate, and the liquid neutral sulphate against contamination by the iron of the trough, flues are provided underneath the trough, through which cooling-air is blown. By this means, and by a suitable depth of the trough, it is possible to produce between the fused mass and the trough a pasty layer.

Garroway (B. P. 6777, 29th March 1899). A mixture of nitre cake with about half its weight of sodium nitrate is heated in a muffle furnace placed on the top of a pyrites burner; a mixture of steam and air is passed into the heated charge, and the vapours containing nitric acid are sent in a continuous stream into the lead chambers used in the manufacture of sulphuric acid, without the

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[1] *Chem. Zeit.*, 1916, p. 571.

intervention of a Glover tower. Or the nitric acid vapours may be condensed and applied in the manufacture of ammonium nitrate and of lead carbonate, as directed in B. P. 2489 of 1896; in B. P. 7066 of 1897; and in B. P. 22395 of 1897. The residue in the furnace from the working is neutral sodium sulphate, suitable for use in glass-making and the like.

Grossmann (B. P. 114180, 19th March 1917). An intimate mixture of nitre cake and sodium nitrate, both finely ground, for instance so as to pass through a sieve having 60 meshes per linear inch, is heated and the resulting gases are mixed with air, which is drawn or blown through the retort or through other parts of the apparatus. Atmospheric or reduced or increased pressure may be employed. The reaction begins at 150° C. and is complete at 250° C., and a practically quantitative yield of nitrogen oxides other than N_2O is obtained. The solid mixture, containing a slight excess of acid, may be conveyed through a retort heated to less than 150° C. at the charging end and about 250° C. at the discharging end. Agitation is unnecessary. The mixture may be placed on trucks previously covered with saltcake or the like to facilitate removal of the product. The trucks may be fed singly by a screw or other pusher from an antechamber provided with sliding doors. At the other end of the furnace is a similar chamber, but with a sloping floor to facilitate the separation of the front truck. Flues from the end chambers may be connected to separate condensers or to the main flue. Muffle furnaces like those used for saltcake, or apparatus like baking ovens, may be employed. Heating may be effected by combustion, waste gas, steam, superheated steam, or superheated water. The nitrogen oxides produced may be passed directly into a vitriol chamber, or may be remixed with steam or a water spray, and the nitric acid condensed. Oxidation and condensation may be done as in the Birkeland-Eyde process.

Freeth (B. P. 117649, 29th June 1917). Sulphuric acid is obtained by causing nitre cake to react with calcium sulphate and water at a suitable temperature, *e.g.* 50 C., filtering off the calcium sodium sulphate and excess of calcium sulphate, cooling the solution to about ordinary temperatures and removing the separated $NaHSO_4$; and then evaporating until the sulphuric acid is of 70 to 75 per cent. strength, cooling to a temperature not above 50° C. but preferably to atmospheric temperature, and separating the $Na_2SO_4, 3H_2SO_4, 2H_2O$. The acid sulphates separated during the process are used again in the next reaction mixture, and the double salt is treated with hot water to separate the Na_2SO_4 from the $CaSO_4$.

Hyatt and Fellowes (B. P. 116181, 6th July 1917). A suitable copper ore, *e.g.* a carbonate ore containing about 5 per cent. of copper carbonate, is added to about its own bulk of a solution of nitre cake containing 3 parts by weight of water to 1 of nitre cake. The mixture is heated at about 100° C. until all the copper is dissolved. The copper is subsequently recovered from the solution by the usual methods, and the sodium salts by evaporation and recrystallisation, or the solution may be neutralised with a suitable carbonate, *e.g.* chalk, sodium carbonate, or, preferably, ammonium carbonate, and used as an insecticide.

J. Grossmann (B. P. 115340, 17th July 1917). Nitre cake is disintegrated or ground at a temperature above ordinary temperature, but considerably below its melting point. The suitable temperatures called the "critical temperature" may be found by heating a sample to temperatures from 40° C. upwards, and testing in a mortar till it readily disintegrates. The nitre cake may be disintegrated at the "critical temperature" and then finely ground at ordinary temperature.

Morgan (B. P. 128302, 27th July 1917). Nitre cake is thrown on to the surface of molten or partially solidified basic slag in a closed chamber. At the temperature of the crust of the slag, 500° to 700° C., oxides of nitrogen and most of the free sulphuric acid are driven off and may be recovered. The residual sulphate is then mixed with the molten slag, by which a temperature of about 1300° C. is attained. The remaining sulphuric acid is thus driven off, chiefly as SO_2, sodium silicate being formed. The gases evolved at this stage are drawn off and utilised in a sulphuric acid chamber or contact plant.

Soc. Industrielle de Produits Chimiques (B. P. 109814, 19th September 1917). Nitre cake is dissolved in water and treated with excess of gaseous ammonia, after which the solution is saturated with carbon dioxide. The precipitated sodium bicarbonate is washed and dried, and the mother liquor, neutralised by nitre cake solution, is diluted and cooled to or below 0° C. to separate the sodium sulphate, and the solution is then concentrated in vacuo or otherwise to recover the ammonium sulphate. The nitre cake may be treated with water to obtain a solution rich in acid which is treated with ammonia, the sodium and ammonium sulphates being separated as above described, and a solid salt poor in acid which, together with the mother liquor from the ammonium sulphate, is treated as above described for the production of sodium bicarbonate and ammonium sulphate.

Grossmann (B. P. 119290, 28th September 1917). The reaction between finely powdered nitre cake and $NaNO_3$ or NaCl to produce

HNO_3 or HCl is effected in the presence of coal, coke, or other carbonaceous matter in fairly large pieces (½ in. diameter or more), in order that the resultant nitre cake shall be friable and easily removable, while the reducing action of the coke, etc., is small. The reaction is carried out as described in patents 111875 and 114180. In making HCl, the temperature may be raised in the later stages to 350° to 450° C.

Dawson (B. P. 127677, 21st November 1917). Nitre cake or other acid sodium sulphate is dissolved in water to obtain a liquor, having a concentration predetermined according to the composition of the acid sodium sulphate and the temperature to which the liquor is to be cooled. The liquor is then cooled to a temperature below 0° C., which effects a separation of Glauber's salt, leaving a mother liquor having a maximum ratio of sulphuric acid to sodium sulphate. If a more concentrated solution is under treatment, cooled water is added during the cooling, in quantity dependent on the original composition of the solution and the degree of cooling. For example, in effecting the separation of Glauber's salt without the addition of water, sodium bisulphate is dissolved to produce a solution of 63° Tw. (sp. gr. 1.315) at 15° C. containing 36 per cent. sodium bisulphate, and approximately corresponding with the molecular formula $H_2O : Na_2SO_4 : H_2SO_4 = 1000 : 425 : 425$. The liquor is refrigerated to $-21°$ C., and the Glauber's salt which separates is removed and washed with cooled water, the wash-liquor being used in the preparation of further solutions of sodium bisulphate. From 10 tons of sodium bisulphate the process produces about 12 tons of Glauber's salt and 15 tons of liquor containing 26.8 per cent. H_2SO_4 and 2.8 per cent. Na_2SO_4.

Bailey, Denny, Norris, and Goold-Adams (B. P. 146546, 5th January 1918). Nitre cake, sodium sulphate, ammonium sulphate, and water are brought together under such conditions that a quantity of anhydrous sodium sulphate is precipitated equivalent to the sodium present in the nitre cake, and, after removal of the precipitate, the liquor is used instead of sulphuric acid to absorb ammonia, *e.g.* from Mond gas, coke-oven gas, or the like. The proportions of nitre cake, sodium sulphate, and ammonium sulphate in the original mixture may either be so adjusted that after absorption of the ammonia and subsequent evaporation of a portion of the water, ammonium-sodium sulphate crystallises out, and after removal of the crystals and further evaporation of a portion of the remaining water, pure ammonium sulphate separates on cooling, or that after absorption of the ammonia and evaporation of a portion of the water pure ammonium sulphate crystallises out, in which case the liquor separated from the crystals is suitable for the treatment of a fresh supply of nitre cake.

Sherwood (U.S. P. 1255474, 5th February 1918). Heat from the combustion of sulphur is utilised to heat nitre cake and effect decomposition of the latter into SO_2 and Na_2SO_4. The Na_2SO_4 is recovered as such and the SO_2 produced by the decomposition and by the combustion is converted into H_2SO_4.

Hart (U.S. P. 1258895, 12th March 1918). Nitre cake is dissolved in water to form a solution of about 1.30 sp. gr., and this solution is cooled to $-40°$ C. to effect crystallisation of sodium sulphate as a granular mass.

Rogé (B. P. 124988, 9th July 1918). About 5 per cent. of pulverised charcoal or sawdust is incorporated with acid sodium sulphate, and the mixture is formed into lumps or slabs which are burned in a kiln with free access of air, the acid gases being collected in the usual manner.

Dawson (B. P. 125311, 11th September 1918). Nitre cake and sulphuric acid are dissolved in water or in the mother liquor obtained in a later stage of the process, and the acid is neutralised with ammonia. The proportion of nitre cake and acid is such that after neutralisation the solution contains ammonium sulphate in excess of sodium sulphate (*e.g.* in the molecular ratio of 2.5 : 1.5). The concentration of the hot solution is adjusted by the addition of water, or by evaporation, to contain 100 to 140 molecules of salt per 1000 molecules of water. On cooling, sodammonium sulphate crystallises. Equivalent quantities of sodium sulphate and sulphuric acid in the form of nitre cake and acid are added to the mother liquor, the concentration of the hot solution obtained is adjusted, and a further quantity of sodammonium sulphate crystals produced by cooling.

Soc. industrielle de Produits Chimiques (B. P. 122172, 23rd December 1918). Alkali chromate solution is treated with carbon dioxide and ammonia, preferably in the presence of ammonium carbonate in excess. Sodium bicarbonate is precipitated and removed, and the solution is then heated to remove ammonia, and ammonium carbonate and lime is added to produce calcium chromate, after which the ammonia liberated is removed by distillation. Nitre cake is then added to produce alkali dichromate and calcium sulphate, the latter being removed by filtration.

Grossmann (U.S. P. 1298334, 25th March 1919; B. P. 12832). NaOH and Na_2SO_4 are produced by mixing nitre cake with calcium sulphite to form soluble compounds in solution and a precipitate, and then reacting on the substances in solution with $Ca(OH)_2$.

Galt (U.S. Ps. (*a*) 1312782, (*b*) 1312783, (*c*) 1312784, 12th August 1919). (*a*) A new material in finely divided form consists of a mechanical mixture of sodium bisulphate and a neutralising base. (*b*) The base may be sodium carbonate. (*c*) The products claimed in *a* and *b* may be added to a lime silica batch, fused, and made into glass.

Kee and Kalbfleisch Corporation (U.S. P. 1313192, 26th August 1919). Nitre cake is heated so that it evolves SO_3 and forms salt-cake. Solid sodium sulphate is then added to cause solidification of the mass.

Shuey (U.S. P. 1293220, 4th February 1919). Mineral or bone phosphate is mixed with about twice its weight of molten nitre cake, and after mixing for one to three minutes, and while the mixture is still fluid, it is withdrawn from the mixing apparatus and allowed to set, cool, and age. About 87 per cent. of the insoluble calcium phosphate originally present in the mixture is converted into mono- and di-calcium phosphates.

Vis (U.S. P. 1294526, 18th February 1919). An aqueous solution of sodium bisulphate is treated with ammonia and then saturated with CO_2 under pressure.

Evans (U.S. P. 1297670, 18th March 1919). An aqueous solution of nitre cake is used for extracting copper from its ores in the form of sulphate. Half as much nitre cake by weight is employed as there is copper to be extracted. A purer copper solution is obtained than with H_2SO_4 alone.

Beveridge (U.S. P. 1315811, 9th September 1919). Nitre cake is heated with carbonaceous material in a non-oxidising atmosphere at a temperature which converts the acid sulphate into normal sulphate. The SO_3 and SO_2 evolved are recovered as sulphuric acid and sulphite respectively.

Banigan and Hercules Powder Co. (U.S. P. 1332195, 2nd March 1920). A mixture of pulverised nitre cake and sodium nitrate is passed in a stream through a rotating tubular retort continuously while subjected to a tumbling movement. Near the discharge end of the stream a higher temperature is maintained than near the inlet end of the apparatus. Nitric acid produced is caused to flow in a direction opposite to the travel of the stream.

Holmes and du Pont (U.S. P. 1354649, 5th October 1920). By continuous treatment of nitre cake with water in such quantities as to prevent complete solution, a solution of 25 to 30 per cent. acidity is obtained.

Acid-Resisting Cement.

Chance and Hunt, A. E. Holley and H. W. Webb (B. P. 110258, 18th October 1917). This invention relates to an improved acid-resisting cement, and has for its object a cement which, while resisting acid, sets sufficiently quickly to be employed for ordinary building purposes.

Ordinary acid-resisting cements usually consist of mixtures of an aqueous solution of sodium silicate with acid-resisting siliceous material.

Cements of this type cannot be employed for ordinary building purposes, as they set slowly, and are not, until partially set, strong enough to support the weight of bricks; they are, moreover, too sticky to work with a trowel.

According to this invention there is added to such known cements 0.5 to 5 per cent. of plaster of Paris, or calcium sulphate, or a mixture of materials forming calcium sulphate.

The aqueous sodium silicate solution employed is preferably about 55° to 65° Tw.

A good example of the improved cement is set out below:—

Ground stoneware passing through a 30 mesh to the linear inch sieve .	8	parts by weight
Fine Leighton sand	7	,, ,,
Ground blue brick passing through a 60 mesh to the linear inch sieve .	2	,, ,,
60° Tw. sodium silicate solution .	3	,, ,,
Plaster of Paris	0.12	,, ,,

The solids are intimately mixed together, a solution of sodium silicate being then mixed with them, either by hand as with ordinary mortar, but preferably from five to ten minutes in an edge runner-mill.

The cement should be used within an hour of making up, and no water or steam should be allowed to come into contact with either the solid constituents forming the cement or with the cement itself, until it is thoroughly dry, and it is therefore desirable to subject the finished work for several days to a temperature of 100° C. or for a shorter time at a higher temperature.

Cements made in accordance with this invention are unaffected by mineral acids or mixtures thereof over a wide range of temperature and by sulphur di-oxide or tri-oxide, nitrous gases, chlorine or sulphuretted hydrogen; they are therefore particularly suitable for the erection of chimneys to take the acid fumes, for reaction and absorbing towers, for acid storage tanks, and in fact for all cases where a good acid-resisting cement is required, and can be applied under suitable conditions.

CHAPTER III

NITRIC ACID MANUFACTURE—ANALYTICAL·

SULPHURIC ACID.

Titration with Alkali.

Preparation of Sample.—The sample is received in a glass-stoppered bottle and is thoroughly mixed by shaking before withdrawing any portion for the purposes of analysis.

Specific Gravity.—A portion of the sample is poured into a hydrometer cylinder and the specific gravity observed by means of a calibrated hydrometer. The hydrometer correction is applied and the specific gravity finally corrected to 15·5° C.

Total Acidity.—The total acidity is determined by titration with normal sodium hydroxide solution using methyl orange as indicator, and the results expressed as sulphuric acid (H_2SO_4).

Varying amounts of the samples are taken so that about 40 or 50 c.c. of normal alkali are required for neutralisation.

For acids of 90 per cent. H_2SO_4 about 2·5 grams are accurately weighed in an oleum bulb (see p. 314), which is then dropped into a titration bottle containing 100 c.c. of distilled water and broken by means of a glass rod, care being taken to ensure that no acid is left in the capillaries of the bulb.

The titration is then carried out by running in normal sodium hydroxide solution from a burette, and the results calculated in the usual way.

NITRIC ACID.

Titration with Alkali.

Preparation of Sample.—The sample is cooled to 15° C. and thoroughly mixed by shaking the bottle.

Specific Gravity.—A portion of the sample is poured into a hydrometer cylinder, and the specific gravity observed by means of a calibrated hydrometer. The hydrometer correction, is applied, and the specific gravity finally corrected to 15·5° C.

Total Acidity.—The total acidity is determined by titration with normal sodium hydroxide solution using methyl orange as indicator.

For strong nitric acid from 2·5 to 3·0 grams are accurately weighed in an oleum bulb (see p. 314), which is then dropped into a titration flask containing from 150 to 200 c.c. of distilled water and broken by means of a glass rod, care being taken to ensure that no acid is left in the capillaries of the bulb. Normal sodium hydroxide is then run in from a burette, and towards the end of the titration two drops of 0·05 per cent. solution of methyl orange are added. It is important that the indicator should be added at the latest possible stage owing to the fact that it is readily destroyed by nitrous acid. The burette is allowed to drain for two minutes and a reading is then taken. Temperature and calibration corrections are applied as described under mixed acids (p. 315) and the result calculated as nitric acid.

Nitrous Acid.—The nitrous acid is determined by titration against a seminormal solution of potassium permanganate.

Ten c.c. of the permanganate solution are pipetted into an Erlenmeyer flask containing 100 c.c. of distilled water which has been acidified with a few drops of sulphuric acid.

The temperature is maintained between 20° and 40° C., and the acid being analysed run in slowly from a burette until a faint permanent pink coloration is obtained.

Nitric Acid.—The percentage of nitric acid is obtained by subtracting the nitrous acid expressed as nitric acid (HNO_3) from the total acidity expressed as nitric acid (HNO_3). For further details, see under mixed acids (p. 313).

Titanous Chloride Method.[1]

When titanous chloride is added to a strong solution of sodium hydroxide, a reaction ensues which results in the precipitation of white titanic hydroxide and the liberation of hydrogen.

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[1] Knecht, *J. Soc. Chem. Ind.*, 1915, **34**, 126-27.

The reaction takes place in two steps according to the equations:—

$$Ti_2Cl_6 + 6NaOH = Ti_2(OH)_6 + 6NaCl \quad . \quad . \quad . \quad (1)$$
$$Ti_2(OH)_6 + 2H_2O = 2Ti(OH)_4 + H_2 \quad . \quad . \quad . \quad . \quad (2)$$

The first reaction results, according to equation (1), in the precipitation of black titanous hydroxide, but this decomposes giving nascent hydrogen and white titanic hydroxide.

If this reaction is carried out in a solution containing nitric acid, the nascent hydrogen produced effects the reduction of the latter, with the formation of ammonia according to equation (3):—

$$HNO_3 + 4H_2 = NH_3 + 3H_2O \quad . \quad . \quad . \quad . \quad (3)$$

The ammonia thus produced may be collected in a known amount of standard acid, and the quantity of nitric acid originally present calculated from the amount of standard acid neutralised.

This method may be used for the determination of nitric acid in such substances as nitre cake.

Procedure.—Twenty grams of the crushed sample of nitre cake are weighed into a distilling flask and approximately 16 grams of caustic soda added, together with 75 c.c. of distilled water. The solution is brought to the boil (a few pieces of granulated zinc being added to prevent bumping), and 20 c.c. of a 15 per cent. solution of titanous chloride added by means of a separating funnel fitted to the flask.

The flask is connected to a Kjeldahl condenser which leads into a receiver containing 20 c.c. of decinormal sulphuric acid.

The liquid is boiled for twenty minutes, after which the flask is disconnected and the acid titrated back with decinormal sodium hydroxide.

Ferrous Ammonium Sulphate Method.

The method for the titration of nitrates by ferrous sulphate described by Bowman and Scott[1] is based upon the fact that when a substance containing nitric acid is titrated with a solution of ferrous sulphate, the latter is oxidised by the acid, and as soon as there is an excess of ferrous iron present it combines with the reduced nitrogen compounds to form

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[1] *Chem. Trade J.*, 25th September 1915.

a red compound, the appearance of this red compound denoting the end point of the reaction.

Bowman and Scott gave the following equation:—

$$4FeSO_4 + 2HNO_3 + 2H_2SO_4 = N_2O_3 + 2Fe_2(SO_4)_3 + 3H_2O.$$

Ferrous ammonium sulphate has been found to be generally more suitable than ferrous sulphate, owing to the fact that an acid solution of the former does not deteriorate so rapidly as one of the latter.

Where nitric and nitrous acids are both present the nitric acid alone is estimated by this method, and the results obtained are identical with those obtained by means of the nitrometer method.

The main drawback is the rapidity with which the standard solution changes with respect to its nitric acid value, which makes it essential that the solution be standardised every day. The change in value does not appear to be very regular and probably depends largely on the amount of air coming into contact with the solution.

Preparation of the Solution.—Fifty grams of ferrous ammonium sulphate are dissolved in 400 c.c. of distilled water. When solution is complete 500 c.c. of cold dilute sulphuric acid (prepared by mixing equal volumes of water and concentrated sulphuric acid) are poured into the solution with thorough stirring throughout the addition. The liquid is cooled and diluted to 1000 c.c. with distilled water. A further 1000 c.c. of cold dilute sulphuric acid (1·1 as before) is then added and the liquid thoroughly mixed by means of a current of air. The strength of the solution is varied according to the use for which it is intended. Thus while the above solution is the most suitable for the estimation of nitric acid in nitre cake, a much stronger solution is desirable for the estimation of nitrogen in nitro-cotton. For this latter purpose 500 grams of ferrous ammonium sulphate are weighed out and the solution then prepared as directed above.

Standardisation of the Solution.—Approximately 100 c.c. of concentrated sulphuric acid are run into a 250 c.c. Erlenmeyer flask, and 10 c.c. of a standard solution of pure potassium nitrate (KNO_3) containing exactly 0·01 gram of nitric acid (HNO_3) per 10 c.c. are added by means of a pipette.

The ferrous ammonium sulphate solution is then run in carefully from a burette, the end point of the titration being indicated by a permanent faint pink coloration.

During the titration the temperature of the liquid is kept below 30° C. by rotating the titration flask in a basin of cold water.

If the 10 c.c. of standard potassium nitrate solution require x c.c. of the ferrous ammonium sulphate solution, then $\frac{0 \cdot 01}{x}$ gram will represent the nitric acid (HNO_3) equivalent of 1 c.c. of the latter solution.

NITRE CAKE.

For plant control purposes it is usually sufficient to determine items 1, 2, and 3 in the following scheme:—

Preparation of Sample.

The sample is roughly broken up and quartered until about one pound remains; the portion is then ground in a mortar as quickly as possible and again quartered so as to leave an analysis sample of about 100 grams.

1. **Total Acidity.**—Five grams are dissolved in water and the solution titrated with normal sodium hydroxide solution, using methyl orange as indicator. The result is expressed as percentage of sulphuric acid (H_2SO_4).

2. **Nitric Acid.**—Five grams of the sample are dissolved in 20 c.c. of water and 100 c.c. of concentrated sulphuric acid added to the solution.

The liquid is then titrated against standardised ferrous ammonium sulphate solution and the result calculated as percentage of nitric acid (HNO_3). A full description of the method of preparation and standardisation of the ferrous ammonium sulphate solution will be found on p. 246.

3. **Nitrous Acid.**—Five grams are weighed out into an Erlenmeyer flask and dissolved in water. Twenty c.c. of $N/100$ potassium permanganate solution are then added and the excess of the latter titrated back with $N/100$ ferrous ammonium sulphate solution. The result is calculated as percentage of nitrous acid (HNO_2).

4. **Total Sulphate.**—The total amount of sulphate present is determined by precipitation as $BaSO_4$; 0·5 to 0·8 gr. is weighed out, dissolved in boiling water, and a boiling solution of $BaCl_2$ added. The precipitate is filtered, washed with hot water, dried, ignited, and weighed.

5. **Insoluble.**—Twenty grams are dissolved in water and the solution filtered through a filter paper previously tared after being dried for two hours at a temperature of 100° C.; the filter paper and residue are then washed several times with hot distilled water and finally dried for two hours in a steam oven. From the gain in weight of the filter paper the percentage of insoluble matter in the nitre cake is calculated.

6. **Iron.**—Twenty grams are dissolved in water and the solution neutralised with normal sodium hydroxide solution. A few drops of ammonium hydroxide are added to the neutralised solution and the solution filtered. The precipitate is washed and then dissolved in dilute sulphuric acid, the solution being collected in a 100 c.c. measuring flask.

Any iron present in the solution is reduced to the ferrous state by adding a small piece of zinc, and after the reaction is complete the solution is diluted to exactly 100 c.c. An aliquot portion of the solution is then withdrawn and titrated with $N/100$ potassium permanganate.

7. **Water.**—By difference, after determining the relative proportions of Na_2SO_4 and $NaHSO_4$, as shown in the following example:—

Example.—

1\. Total acidity . . . (as H_2SO_4) = 1·42
2 and 3. Nitrogen acids . . . („) = ·005
Acidity due to $NaHSO_4$. („) = 1·415
∴ SO_4 in $NaHSO_4$. . . („) = 2·830 (*a*)
(on 5 grams nitre cake).

4\. SO_4 content of total sulphate (as H_2SO_4) = 3·82
„ „ $NaHSO_4$. („) = 2·83 (*a*)
„ „ Na_2SO_4 . („) = 0·99 (*b*)
(calculated to 5 grams nitre cake).

$$\text{The } NaHSO_4 \text{ content, as such} = 2{\cdot}83\,(a) \times \frac{120}{98} = 3{\cdot}47$$

$$\text{The } Na_2SO_4 \text{ content, as such} = {\cdot}99 \times \frac{142}{98} = 1{\cdot}43$$

The complete analysis of the nitre cake thus becomes:—

Na_2SO_4 . . . . . = 1·43 × 20 = 28·6 per cent.
$NaHSO_4$ . . . . . = 3·47 × 20 = 69·4 „
2 and 3. Nitrogen acids (as HNO_3) = ·003 × 20 = ·06 „
5. Insoluble . . . . . = ·04 × 5 = ·2 „
6. Iron . . (as Fe_2O_3) = ·06 × 5 = ·3 „
7. Water . . . . . (by difference) = 1·44 „
100·

Alternative Method for Total Sulphate.

The neutral solution resulting from (1) is evaporated to dryness on a water-bath in a silica basin. The residue is dried in a water oven and then heated to *dull redness* over a naked Bunsen flame, till it ceases to lose weight. The resulting product is Na_2SO_4 and is estimated as H_2SO_4

$$(Na_2SO_4 \times 0.69 = H_2SO_4)$$

CONSTITUTION OF NITRE CAKE.[1]

Nitre cakes of more than 18·7 per cent. acidity consist of a mixture of sodium hydrogen sulphate and the compound $Na_2SO_4 . NaHSO_4$.

Cakes of less than 18·7 per cent. acidity comprise a mixture of sodium sulphate and the compound $Na_2SO_4 . NaHSO_4$, and contain no sulphuric acid.

A cake of 18·7 per cent. acidity consists of the compound $Na_2SO_4 . NaHSO_4$ and contains neither sodium sulphate nor sulphuric acid.

The molecular proportions of a nitre cake of known acidity may be calculated from one of the two formulæ given below:—

(*a*) If acidity is less than 18·7 per cent.:—

$$x = 1 - \frac{142y}{4900 - 120y},$$

where

x = molecular proportion of Na_2SO_4.
$1 - x$ = molecular proportion of the compound $Na_2SO_4 . NaHSO_4$.
y = acidity as per cent. H_2SO_4.

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[1] Butler and Dunnicliff, *J. Chem. Soc. Trans.*, 1920, **117**, 666.

(*b*) If acidity is 18·7 per cent. or more, but not greater than 40·83 per cent.:—

$$x = \frac{4900 - 120y}{142y},$$

where

x = molecular proportion of the compound $Na_2SO_4 . NaHSO_4$.
$1 - x$ = molecular proportion of $NaHSO_4$ in the nitre cake.
y = acidity as per cent. H_2SO_4.

CHAPTER IV

DENITRATION OF WASTE OR SPENT MIXED ACIDS

Spent Acids.

In processes where organic substances are nitrated by using mixtures of nitric and sulphuric acids, a residual mixed acid is usually obtained containing a much lower percentage of nitric acid mixed with sulphuric acid and diluted with water. Such a mixed acid is known as a waste, spent, or refuse acid. Formerly the nitric acid content of such acids was wasted, although the sulphuric acid content was again made available by a process of concentration. During this concentration process the nitric acid was eliminated to atmosphere. Fortunately such waste is now a thing of the past, and both nitric and sulphuric acids are recovered for use again in the nitrating process.

Separation of Constituents—Denitration.

1. **By Simple Distillation.**—In the denitration of spent acid from nitration of cotton it is possible to regain concentrated nitric acid and dilute sulphuric acid by simple distillation as already described (p. 178).

In denitrating many other waste acids, both sulphuric and nitric acids when separated are considerably diluted with water.

2. **By Steam.**—A simple and much used process of denitration depends upon the introduction of steam to the bottom of some column or box apparatus down which spent acid flows over suitable packing material. Nitric acid vapours pass away at the top of the apparatus and denitrated sulphuric acid flows from the base. Liberation of nitric acid is facilitated by dilution of the sulphuric acid, as dilute sulphuric acid does not retain nitric and nitrous acids so well as the concentrated acid.

3. **By Hot Air and Steam.**—Occasionally a mixture of heated air and steam is used for denitration in place of steam alone.

In processes 2 and 3 the nitric acid vapours are passed forward to a condensing and absorbing system as described under nitric acid manufacture, while the hot denitrated sulphuric acid is delivered from the base of the column into a suitable cooler before passing to storage.

As the nitric acid content of spent nitrating acids is in contact with much organic matter, it is often very much reduced to lower states of oxidation, and the direct yield of nitric acid from a denitrating tower may be very small, the chief recovery of nitric acid being dependent upon an efficient absorption system for conversion of lower oxides of nitrogen into nitric acid.

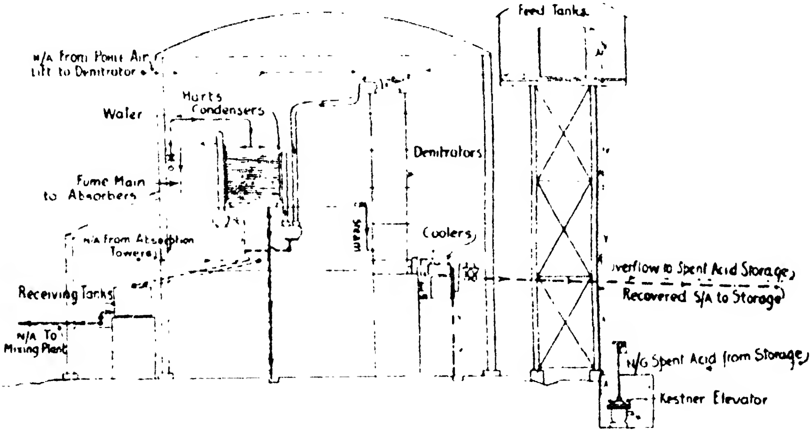

FIG. 100.—Section through Denitrating House, H.M. Factory, Gretna.

NITRO-GLYCERINE SPENT ACID.

The Plant.

A plant for the denitration of this mixed acid may consist of the following parts :—

1. Storage accommodation for spent acid.
2. Delivery system for conveying spent acid to denitration column.

3. Denitration column.
4. Nitric acid recovery system, including condensing and absorption systems.
5. Denitrated sulphuric acid cooling and receiving system.
6. Steam supply.
7. Building to house the plant.

Fig. 100 is a diagrammatic representation of such a plant.

Storage of Spent Acid.

The spent acid is conveniently stored in lead-lined wood tanks, each provided with a perforated lead pipe along the bottom to supply air for agitation when necessary. There is always a possibility of traces of nitro-glycerine separating out from the spent acid, and it is advisable to watch for this happening and to guard against its accumulation by stirring it in with the acid going forward for denitration. Air agitation is useful at such times.

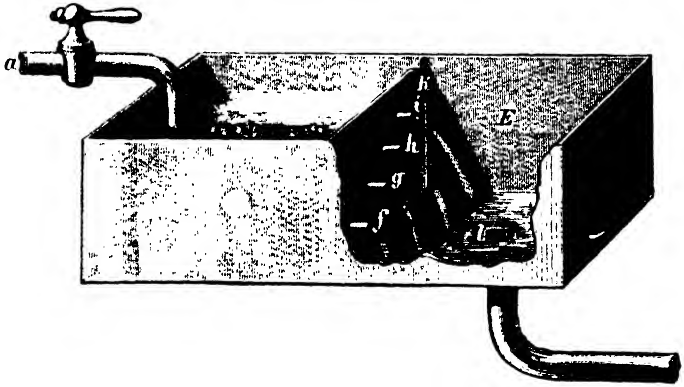

FIG. 101.—Acid Feed Box.

Delivery of Spent Acid to Denitration Column.

If the store of spent acid is situated at a low level it may be lifted to small supply tanks above the top of the denitrating column before being fed to the latter. The lead-lined Kestner automatic elevator serves very well for lifting nitro-glycerine spent acid through lead service lines.

A small lead feed box having a baffle with a series of holes at different levels along a diagonal line serves sufficiently well to regulate the supply of acid to the tower, control to the feed box being effected by a regulus or earthenware cock.

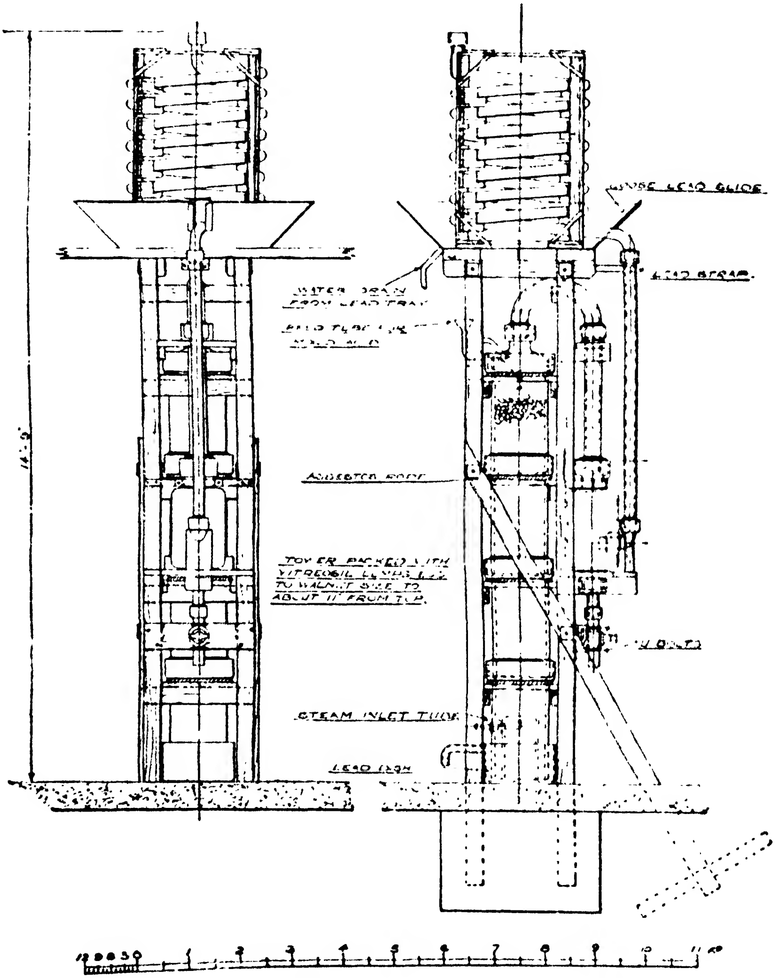

FIG. 102.—Denitrating Tower (Thermal Syndicate).

***Author's Note.*—Lead trays, straps, etc., should be avoided where dilute nitric acid is being handled. Earthenware trays and wood supports are more suitable.**

The Denitration Column.

The denitration column is usually from 8 to 15 ft. high and may be of silica ware or acid-resisting iron spigot and socket

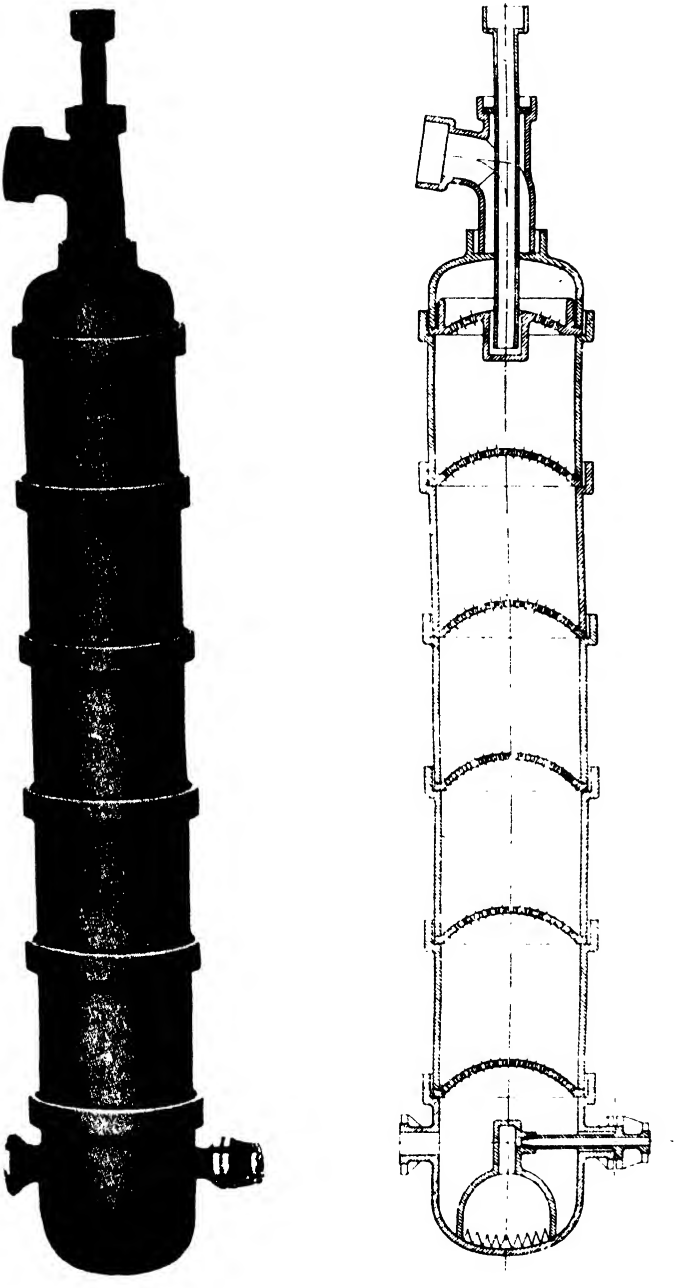

FIG. 103.—"Narki" Metal Denitrating Tower.

pipes; of pottery ware pipes having an outer casing of flanged steel pipes protected from acid by a packing of a barium sulphate and tar mixture, 6 to 1, rammed in hot, or one of powdered glass and silicate of soda solution, 4 to 1; or of acid-proof bricks. In any case the bottom section is usually of thick lead provided with a hole for the introduction of a steam supply pipe and an outlet for the denitrated sulphuric acid. It is convenient to have a thermometer resting in the outflowing acid to register its temperature.

The column is packed with graded quartz from 4 in. to ½ in. size, or special packing, which rests on a chequer-work brick support so arranged to give a free opening for the steam blower. On the top of the finest quartz a silica or Ceratherm ware distributing plate rests in order to provide an even distribution of the acid. The column stands in a lead tray which rests on a brick support at a suitable elevation to give gravity flow of denitrated acid to store.

An interesting and effective denitration column was introduced at H.M. Factory, Craigleith, during the war by J. W. Romanes, an illustration of which is given in Fig. 104. It was built of acid-proof brick and stood only 6 ft. high. Intimate contact between the steam introduced at the bottom and the mixed acid to be denitrated was obtained by introducing perforated earthenware tiles at intervals, successive tiles being connected by pieces of earthenware pipe. The bubbling and scrubbing effect produced proved to give a very satisfactory denitration.

Nitric Acid Recovery.

From above the distributing plate a gas take-off leads the nitric acid vapours and nitrogen oxides to the condensing system, from where the uncondensed gases are drawn through the absorption system by some fume exhaustion device as outlined under nitric acid manufacture.

Sulphuric Acid Recovery.

The denitrated sulphuric acid leaving the base of the column is passed through a lead cooler of suitable capacity before being carried by a lead-pipe line to a lead-lined wooden tank for storage purposes.

Steam Supply.

Steam is supplied to the column under pressure by means of an acid-resisting iron perforated pipe, which is fixed into the lead base pipe with blue asbestos cord and soft asbestos putty coated with hard silicate putty. Either ordinary saturated steam or superheated steam may be used for the purpose of denitration.

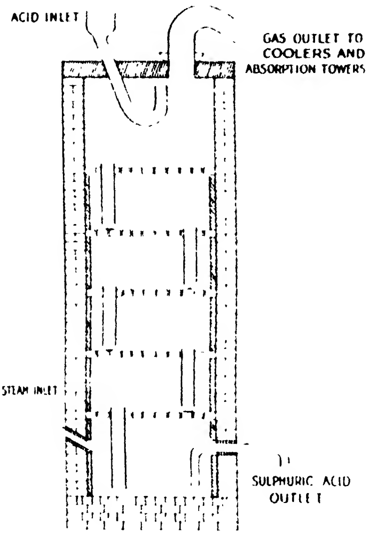

FIG. 104.—Denitrating Tower, H.M. Factory, Craigleith.

Enclosing Building.

A simple structure of wood over a steel framework may be used as an enclosing building for all the plant except the absorption system, which should be open to the air.

The Process.

Successful denitration depends on supplying just the correct quantity of steam to bring about complete separation of the nitric and sulphuric acids from the mixture, and to decompose the nitro-glycerine present. Occasional tests for nitric acid are made on the issuing sulphuric acid by the use of ferrous sulphate solution.

Working Results.—The following are typical working results at H.M. Factory, Gretna:—

Composition of nitro-glycerine spent acid, H_2SO_4 = 75·0 approx.
T.N.A. (as HNO_3) = 8·5 (by nitrometer)
H_2O = 16·5 „
100·0

Pressure of steam	100 lb. per sq. in.
Temperature of steam	170° C.
Temperature of gases leaving column	90° to 95° C.
„ of acid „	150° to 155° C.
Average strength of nitric acid	56 to 60 per cent. HNO_3
„ of sulphuric acid	73 to 74 „ H_2SO_4
Steam usage	0·13 ton per ton of spent acid
Average recovery of nitric acid	97 per cent.
„ of sulphuric acid	99·7 „

The Nitrous Gases.

About 2·5 per cent. of nitro-glycerine is always present in solution in the spent acid, and decomposition of this nitro-glycerine by the steam causes the reduction of about 50 per cent. of the nitric acid present to nitric oxide, nitrogen peroxide, and nitrogen. Decomposition of the organic matter results in the production of carbon monoxide and carbon dioxide, which pass forward with the nitrous gases. The composition of the gases leaving the denitration column is represented by the following analysis, though it varies very considerably.

Composition before Condensation—

HNO_3	26·7 per cent. by weight
NO_2	15·4 „ „
NO	7·8 „ „
H_2O	34·6 „ „
CO_2	5·9 „ „
CO and N_2	9·6 „ „
	100·0

Importance of Absorption.—It is thus seen that success in complete recovery of the nitrogen content of the spent acid entering the denitration column as nitric acid largely depends on the efficient production of nitric acid from nitric oxide and nitrogen peroxide in the absorption system. The immediate condensation of the nitric acid vapour presents no difficulties.

Condensation.—In the condenser attached to the denitration column the greater part of the steam and nitric acid in the gases is removed, and a dilute nitric acid (strength being dependent on steam conditions, *e.g.*, whether superheated or not) is condensed. Using saturated steam at 170° C. the nitric acid condensate at Gretna was about 40 per cent. HNO_3, and was afterwards concentrated to about 60 per cent. by being passed forward to the absorption system where it was circulated. The following analytical figures show the composition of the gases leaving the condensing system:—

Composition after Condensation—

	Percentage by Weight.	Percentage by Volume.	Percentage of Total Combined Nitrogen.
HNO_3	5·4	3·1	6·6
NO_2	36·6	24·4	61·3
NO	12·4	15·5	32·1
H_2O	4·9	9·8	...
CO_2	9·3	7·8	...
O_2	1·3	1·7	...
N_2+CO	30·1	37·7	...
	100·0	100·0	100·0

The gases are seen to be concentrated in regard to nitrogen compounds (43 per cent.), whereas the oxygen content is very small (1·7 per cent.). For oxidation of the nitric oxide throughout the absorption process, an adequate supply of oxygen has to be provided. Using Pohle air lifts and carrying the exhausted air back to the system, sufficient oxygen is provided by the air thus introduced to the system to bring about efficient oxidation.

Reactions in the Absorption Process.—Absorption of nitrous fumes by water is brought about mainly by reactions represented by the following equations:—

$$(1)\ 3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$$

$$(2)\ 2NO + O_2 = 2NO_2$$

Conditions for Successful Absorption.—The amount of conversion of NO_2 to HNO_3 depends on the velocities of the reactions represented by the above equations, and is controlled largely by that of reaction 2 which is relatively slow. Ample time for reaction should therefore be provided.

PACKING MATERIALS.—Close packing of the absorbing towers reduces the gas space capacity of the system, and therefore is equivalent to increasing the velocity of the gases. The use of quartz and such like packings is thus seen to be disadvantageous for absorption purposes. An open packing material which gives maximum free gas space with adequate wetted surface should be chosen, and many patent tower packings developed with these points in view are available.

AIR SUPPLY.—The use of an excess of air beyond what is necessary for oxidation purposes also reduces the reaction time available in the system for conversion of nitrous fumes, and is therefore to be avoided.

From equation 2 above it is seen that the velocity of oxidation of NO is proportional to the concentration of O_2 and to the square of the concentration of NO. The great influence of NO concentration on its rate of oxidation is well known. As long as the concentration of NO is relatively high the maximum rate of reaction is attained with comparatively little admixed air, but with low concentrations of NO the air requirement for maximum rate of reaction becomes much larger. For best efficiency, therefore, it would appear necessary to add air at many points in the absorption system, and this is accomplished by use of the air lift.

WATER SUPPLY.—Lack of water supply (as dilute nitric acid) in the absorption system naturally leads to inefficient absorption. The total water content is influenced by the necessity to produce as strong a nitric acid as possible, but rapidity of circulation by the Pohle lifts gives the opportunity for sufficient water contact. A too rapid circulation of water, however, will tend to produce the same effect as close packing, and so reduce the time of gas contact.

The absorption process may be worked to give a recovery of 94 to 97 per cent. of the combined nitrogen entering the system.

The process of denitration of nitro-glycerine spent acid with subsequent recovery of nitric acid was closely investigated at H.M. Factory, Gretna, and a summary of a report on the process in general, with special reference to absorption, is given at a later stage (p. 265) as an indication of the problems met with in denitration.

Analysis of Nitro-glycerine Spent Acid.

Total Nitrogen Acids.—The total nitrogen acids are estimated by means of the nitrometer in the manner described for other mixed acids (p. 259), and the results expressed as nitric acid (HNO_3). The approximate quantity needed to give the desired volume of gas in the nitrometer is from 3·0 to 3·5 grams, and this is weighed in a Lunge-Rey pipette which has previously been washed out with a portion of the sample.

The percentage of nitric acid determined in this way includes the nitric acid present in the spent acid as nitric esters, etc., but as acid combined in this way is recovered in the denitration process, the method adopted is considered to give a fair indication of the available nitrogen acids.

Sulphuric Acid.—The percentage of sulphuric acid is determined by titration of the spent acid with normal sodium hydroxide solution, after freeing the sample from total nitrogen acids by evaporation.

About 3·5 grams of the acid are accurately weighed out into a shallow porcelain evaporating basin, by means of a Lunge-Rey pipette. A few cubic centimetres of water are added and the liquid evaporated in a steam-bath for from two to three hours, more water being added about every half hour. To free the liquid from nitric acid quickly, it is essential to evaporate down to the smallest possible bulk each time before the addition of a further quantity of water is made. When it is considered that the liquid is completely freed of nitrogen acids, the remaining sulphuric acid is diluted, carefully washed into a titration flask, and titrated against normal sodium hydroxide using methyl orange as indicator. As there is little indication to show when all the nitric acid has been driven off, the determination is always carried out in duplicate. From the number of cubic centimetres of normal alkali required for neutralisation, the percentage of sulphuric acid (H_2SO_4) present in the sample is calculated.

Water.—The percentage of water present in the spent acid is obtained by difference, that is, by subtracting the sum of the total nitrogen acids and sulphuric acid from 100.

Note.—**Nitric and Sulphuric Acid Esters.**—Nitro-glycerine spent acid contains in solution nitric acid esters (including mono-, di-, and tri- nitro-glycerines) and sulphuric acid esters in small quantities.

If the normal analytical determination of total acidity of a mixed acid is made with nitro-glycerine spent acid, the result does not include the combined acids represented by the esters content. In the nitrometer determination of total nitrogen acids, however, the nitric esters are decomposed with formation of nitric oxide, and the resulting nitric acid figure therefore includes a combined nitric acid content not included in the total acidity determination. Subtraction of nitrometer nitric acid from total acidity thus results in a too low percentage of sulphuric acid.

This difficulty is overcome by determining the percentage of sulphuric acid by titration after the nitrogen acids have been driven off by evaporation.

The nitrometer determination gives the potential nitric acid content of the spent acid, but since in the denitration process the nitric esters are decomposed and their nitrogen content is ultimately recovered as nitric acid, the determination gives a reliable indication of the available nitric acid. Sulphuric acid esters are possibly hydrolysed during the evaporation method for determination of sulphuric acid, and therefore the final analytical results are no doubt representative of the available acid content of the spent acid.

In a report on the Analysis of Nitro-glycerine Waste Acid (undated) by W. O. Jones, at H.M. Factory, Pembrey, the author concludes that the most accurate method of analysis is by the total acidity method, and subsequent deduction of total nitrogen acids, a correction being applied for the nitric esters and sulphuric esters present after estimation of these by chloroform extraction.

Jones carried out the chloroform extraction and subsequent determination as follows:—The spent acid was extracted rapidly with chloroform and the chloroform evaporated by allowing a current of air to play on the surface of the liquid. The nitric esters in the residue were determined by nitrometer. The sulphuric esters were determined on a fresh sample by drowning the chloroform extraction residue in warm water, warming on a water-bath, and adding concentrated nitric acid from time to time. Finally, concentated hydrochloric acid and a crystal of potassium chlorate were added and all the nitric acid driven off by evaporation to a small bulk. Sulphuric acid was now determined by addition of barium chloride in the usual manner.

T.N.T. SPENT ACID.

The Process.

The process used is fundamentally the same as for nitroglycerine spent acid, although slight modifications are necessary here and there.

Nitro-Bodies. — An approximate composition of T.N.T. spent acid is:—

H_2SO_4	72·5 per cent.
T N.A.	4·5 ,,
H_2O	23·0 ,,

but it carries with it varying quantities of organic nitro-bodies such as mono-, di-, and tri-nitrotoluol. A portion of these nitro-bodies can be removed from the surface of the spent acid at rest in the store tanks although some goes forward to the denitration process. From the denitration column the nitro-bodies pass forward undecomposed with the nitric acid vapours and are condensed along with dilute nitric acid. It is advisable to instal some settling system at this point, so that the nitro-bodies may settle out while the dilute nitric acid is allowed to pass forward to be used as circulating liquid in the absorption system.

Practice at H.M. Factory, Queen's Ferry, involved further dilution of the condensed dilute nitric acid from 28 per cent. HNO_3 to about 15 per cent. HNO_3 (sp. gr. less than 1·120), in order to ensure satisfactory separation of the nitro-bodies which were then settled out in a series of Woulff's bottles. Periodically the nitro-bodies were run off to a receiver, washed with water, and returned to the nitration department along with spent acid tank skimmings.

Admission of Air. — Another feature of Queen's Ferry

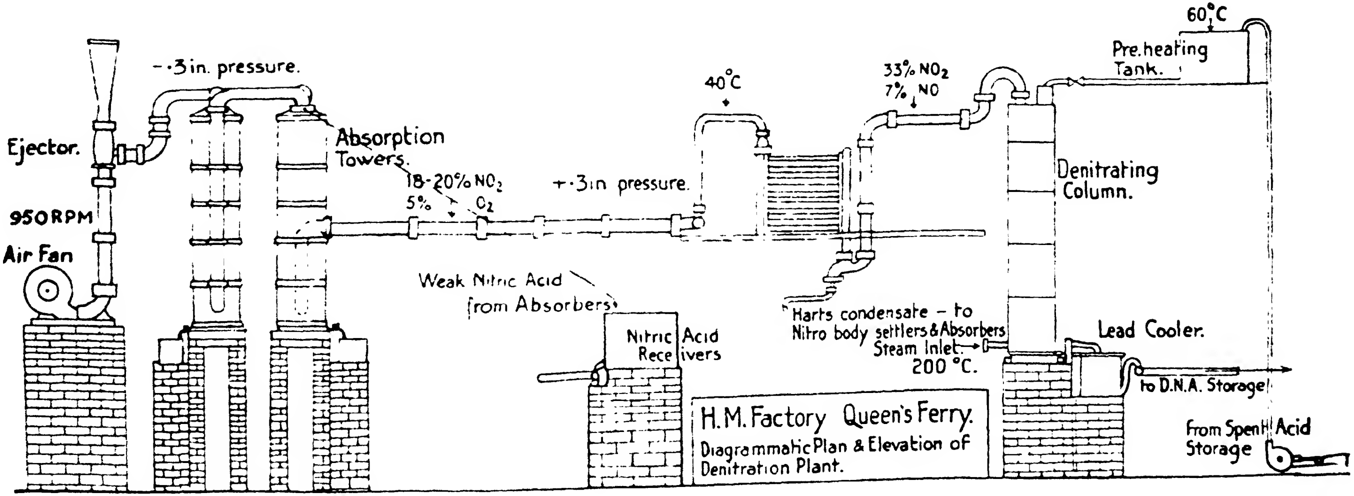
60°C
Pre.heating Tank.
-·3in. pressure.
Ejector.
950RPM
Air Fan
Absorption Towers.
18-20% NO₂
5% O₂
+·3in pressure.
40°C
33% NO₂
7% NO
Denitrating Column.
Weak Nitric Acid from Absorbers
Nitric Acid Receivers
Harts condensate – to Nitro body settlers & Absorbers
Steam Inlet
200 °C.
Lead Cooler.
to D.N.A. Storage
From Spent Acid Storage
H.M. Factory Queen's Ferry.
Diagrammatic Plan & Elevation of Denitration Plant.

FIG. 105.

practice was the introduction of air by means of a Narki metal jet into the fume main carrying gases from the condensers to the absorbing towers. This jet caused sufficient suction at the head of the denitration column to admit air required for oxidation of nitric oxide before the condensers, and provided additional air for oxidation purposes in the absorption system.

Plant Lay-out.

Figs. 105 and 106 give diagrammatic representations of T.N.T. denitration plant lay-out at H.M. Factories, Queen's Ferry and Craigleith respectively.

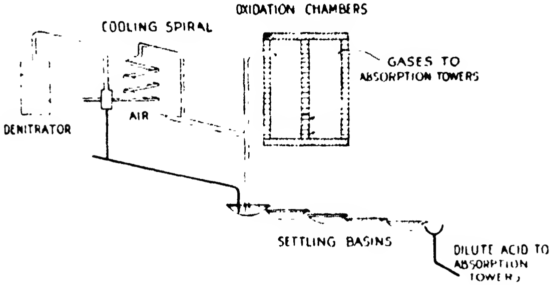

FIG. 106.—Diagrammatic Lay-out of Denitration Plant (H.M. Factory, Craigleith).

Working Conditions.

The following summary of an investigation into the best conditions for recovery of nitric acid in denitration of T.N.T. spent acid is given in an undated report from H.M. Factory, Queen's Ferry.

1. Sufficient air should be admitted (by suction) to the top of the denitration column for the oxidation of all the nitric oxide present in the gases.

2. The heat evolved in this oxidation, along with the sensible heat of the rest of the gases, should be removed by proper operation of the condensers.

3. The gases leaving the condensers should consist only of nitrogen peroxide, nitrogen, and excess air.

4. The nitro-body should be removed from the condensed nitric acid, which is then to be passed forward and fed along

with a sufficient supply of water into the last absorption tower of the series. The acid is then worked forward through the absorption system, meeting gases richer and richer in NO_2, and finally run off to storage on reaching a strength of 50 to 55 per cent. HNO_3.

5. The Pohle air lifts serve three purposes:—

(*a*) To elevate the acid.
(*b*) To cool the acid.
(*c*) To promote oxidation of HNO_2 produced on solution of NO_2 in water.

6. The optimum temperature in the absorption process is 35° to 40° C.

7. The velocity of the gases through the whole system should be as low as possible.

8. The maximum amount of packing should be provided in the absorbing towers, providing the gas velocity is not thereby unduly accelerated.

The Absorption Process.

Air Supply.—In Technical Research Report No. 16, H.M. Factory, Oldbury, on Improvements in Recovery of Nitric Acid from Denitrator Absorber Towers, H. W. Webb shows that lack of sufficient air in the system for oxidation purposes favours the right to left reaction represented in the equation—

$$6NO_2 + 3H_2O \rightleftharpoons 4HNO_3 + 2NO + H_2O.$$

Nitric oxide and peroxide interact to give nitrogen trioxide, which dissolves in the nitric acid, failing oxygen for further oxidation—

$$NO + NO_2 = N_2O_3.$$

The nitric acid solution is thus coloured bluish green due to the presence of N_2O_3 in solution.

With addition of a proper supply of oxygen further oxidation is effected and the bluish green coloration gives way to the yellow colour due to the presence of NO_2.

Water Supply.—Webb also records a series of experiments showing the effect of shortage of water-feed to an absorbing system in causing production of nitric acid of maximum concentration to take place in different towers of the series used. The following figures show this:—

Water-Feed.	Number of Tower containing acid of greatest HNO_3 Concentration (counting from the gas inlet).
4 gallons per hour	No. 7
8·5 " "	" 5
13 " "	" 3
17 " "	" 2
20 " "	" 1

SUMMARISED REPORT ON AN INVESTIGATION OF THE DENITRATION OF NITRO-GLYCERINE SPENT ACID.[1]

Objective.—To investigate the composition of the gases throughout the denitration plant, and to study the conditions giving most efficient recovery of nitric acid.

Results of Work.—1. The oxides of nitrogen leaving the denitrator have the average composition N : O : : 1 : 2 and the gases contain NO, NO_2, and HNO_3.

2. The carbon of the spent acid is converted into dioxide and monoxide according to volume ratio CO_2 : CO : : 1·75 (to 1·6) : 1.

3. The gases leaving the Hart's condensers contain over 40 per cent. by volume of nitrogen oxides and only traces of oxygen. The total nitrogen is distributed as follows: 6·6 per cent. as HNO_3, 61·3 per cent. as NO_2, and 32·1 per cent. as NO.

4. Admission of air at the top of the denitrators raises the temperature of the gases leaving the Hart's condensers, but does not increase the amount of total nitrogen condensed as HNO_3 in the Hart's.

5. The proportion of NO is from 1 to 3 per cent. in the central towers of a battery. The percentage of combined nitrogen as NO decreases as the gases pass through the first two towers and then increases towards the exit; the chief loss of combined nitrogen at the exit is as NO.

6. In the first one or two towers of each battery, NO is proportionately more rapidly oxidised than it is formed by the decomposition of HNO_2; in the later towers the reverse

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[1] H.M. Factory, Gretna, Experimental Report No. 108 (Dornock), 17th July 1918, by A. Geake, J. D. M. Dunbar, and F. J. Squire.

is the case, so that the function of these is to oxidise NO and absorb the resulting peroxide.

7. Conditions giving efficient absorption of NO_2 are maximum area of wetted surface, and maximum concentration of NO_2. These conditions can be attained by the use of a packing which gives a large area of wetted surface without occupying excessive space, *e.g.*, Accrington ring packing, and by reducing the volume of air admitted to the minimum required for oxidation.

8. Conditions giving efficient oxidation of NO are (*a*) maximum free space, and (*b*) maximum concentration of NO, and can be attained by using as little packing as possible, *e.g.*, the outer cylinders only of Accrington ring packing, and by admitting the minimum volume of air.

9. The empty towers (No. 4 of Battery I. and No. 5 of Battery II. during the test runs) compared favourably with the packed towers as regards absorption of total combined nitrogen either as NO or NO_2.

10. In the first few towers of each battery absorption of NO_2 requires to be promoted, and in the later towers the oxidation of NO. The first four towers should therefore be packed with the complete Accrington ring packing, and the last four only with the outer cylinders of this packing.

11. Air admitted through the Pohle lifts is sufficient to oxidise the nitrous fumes; air admission from other sources should, therefore, be avoided.

12. The maximum concentration of acid obtainable in the absorbers is about 60 per cent. HNO_3.

Recommendations.—1. *Packing of Towers.* (*a*) Towers 1 to 4 of each battery should be packed with complete Accrington ring packing.

(*b*) Towers 5 to 8 of each battery should be packed with the outer cylinders only of Accrington ring packing.

(2) *Air Admission.*—The volume of air admitted, except through the Pohle air lifts, should be the minimum possible When only one or two denitrating columns are in use this can be best carried out by reducing the suction of the fan.

Experimental.—The analytical and sampling methods employed are fully dealt with in Gretna Experimental Report, No. 96 (D.)[1]

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1919, **38**, 367-69.

REFERENCES.

Denitration.

POHL.—*Z. angew. Chem.*, 1912, p. 1853.

LEMAÎTRE.—*Monit. Scient.*, 1913, pp. 217-30.

MILES.—*Amer. Inst. Chem. Eng.*, 1917; *J. Ind. Eng. Chem.*, 1917, **9**, 164-5.

A. GEAKE AND F. J. SQUIRE.—*J. Soc. Chem. Ind.* (*Trans.*), 1919, **38**, 367-9.

CHWALA.—*Œsterr. Chem. Zeit.*, 1920, **23**, 90-3; *J. Amer. Chem. Soc. Abstr.*, 1920, **14**, 2988.

E. GALLE.—*Z. angew. Chem.*, 1921, **34**, 168-70, 173-5; *J. Soc. Chem. Ind. Abstr.*, 1921, **40**, 385.

DENITRATION OF SPENT ACIDS.—"Technical Records of Explosives Supply, 1915-18, No. 4, H.M. Stationery Office."

PATENTS.

Denitration.

Hirsch (Ger. P. 46096) runs the impure acid through a stoneware worm, placed in water of 80° C. Air is blown in at the bottom, and the feed of nitric acid is so regulated that it runs out at the bottom at a temperature of 60° C. and sufficiently bleached. It runs through a second worm placed in cold water, and can then be put into the carboys. The nitrous gases escaping at the top of the first worm are treated in the usual manner. One worm can purify several tons of acid per diem. The same process may also serve for treating the waste acid of nitro-glycerine and nitro-benzene works; in this case air heated to 150° C. or steam is blown in at the bottom, and the feed of acid is so regulated that it issues, at a temperature of 140° C., as comparatively pure sulphuric acid.

Kaesemacher (B. P. 2382, 1908; Fr. P. 386783) separates the acids, concentrating them at the same time, by the old process of running them down a tower, filled with acid-proof materials, in which hot air ascends.

Hechenbleikner (U.S. P. 1264512, 30th April 1918; Can. P. 191311, July 1919). Sulphuric acid to be denitrated is sprayed into a flowing stream of steam, and oxygen is introduced into the resulting gases. Nitric acid fumes are thus formed and condensed.

Baer (Ger. P. 323416, 27th February 1919). A denitration plant comprises a tower built up of sections with superposed, perforated plates arranged internally at 5 to 7.5 mm. distance from the walls. The plates have large central openings for the passage of nitrous vapours, and smaller ones for the sulphuric acid flow, with partition walls between the sets of openings dividing the plates into two parts.

CHAPTER V

MIXED ACIDS

Contractions used.

T.N.A. = Total Nitrogen Acids (expressed as HNO_3).
S.A. = Sulphuric Acid.
N.A. = Nitric Acid.
S.N.A. = Strong Nitric Acid.
W.N.A. = Weak Nitric Acid.
M.A. = Mixed Acid.
R.V.A. = Revivifying Acid.
N.G. = Nitro-glycerine.
N.Co = Nitro-cotton.

INTRODUCTION.

FOR the purposes of this work the mixed acids to be considered are those made with nitric and sulphuric acids as constituents. They are specially important as being necessary for the production of a large number of nitrated organic compounds used as explosives, and as bases for many industrial products. Such mixed acids are necessary for the manufacture of the following important substances:—

1. Nitro-glycerine.
2. Gun-cotton.
3. Picric Acid.
4. Tri-nitro-toluene (T.N.T.)
5. Nitro-cotton for explosives.
   „ „ celluloid.
   „ „ collodion.
   „ „ artificial silk.
6. Many of the so-called "Intermediates" of the coal tar dye industry.

The explosives industry is a great user of mixed acids, and during the recent war preparation of such acids was developed on an enormous scale. The information available to the author is mainly a result of war-time explosives manufacture, but the principles and practice of mixing to be outlined are of universal application.

COMPOSITION.

The proportions of H_2SO_4, HNO_3, and H_2O in mixed acids vary very considerably and depend on such factors as—

1. The nature of the substance to be nitrated; and
2. The nitrogen content required in the compound to be formed.

The question of composition will not be dealt with further than by providing typical compositions worked to for the preparation of various important nitrated bodies. Such are:—

Nitrated Body.	Composition of Mixed Acid used.		
	H_2SO_4.	HNO_3.	H_2O.
Nitro-glycerine 1	58·5	40·4	1·1
Nitro-glycerine 2	58·4	40·0	1·6
Nitro-glycerine 3	52·5	46·5	1·0
Gun-cotton 1	74·0	18·6	7·4
Gun-cotton 2	70·5	21·6	7·9
Gun-cotton 3	69·35	23·15	7·5
Mono-nitro-toluene (M.N.T.)	62·0	21·2	16·8
Tri-nitro-toluene (T.N.T.) from M.N.T.	79·5	17·8	2·7
Nitro-cellulose :—			
(*a*) for Cordite	62·15	23·0	14·85
(*b*) for Celluloid 1	44·7	35·4	19·9
(*b*) for Celluloid 2	61·1	24·5	14·4

PREPARATION.

The actual preparation of mixed acids is not a difficult operation. It involves a stirring together of the acids forming the mix, and the plant necessary need consist only of tanks of appropriate capacity made of suitable material and provided with facilities for agitation.

The complete process of mixing, however, is somewhat more extensive, and may be considered under the following heads:—

1. Receipt of raw acids.
2. Actual mixing.
3. Delivery of finished products.
4. Blending.
5. Storing.

Raw Acids.

The raw acids may have to be chosen from the following:—

1. Sulphuric acid of all strengths.
2. Oleum of all strengths.
3. Nitric acid of all strengths.
4. Mixed acids returned as spent acids from nitration processes.

Where possible, of course, it is advisable to work with a small number of acids of regular composition. This facilitates and simplifies the mixing process.

Receipt of Raw Acids.

In a self-contained factory where all the necessary acids are available on the site, it is a good plan to arrange gravity flow for all ingredients to the mixing station. The great convenience of this system makes it advisable to adopt the same practice even if the raw acids have to be imported. This can be done by having an elevated storage system into which the imported acids can be delivered and from which they can be drawn for mixing purposes as required. Apart from other considerations, the adoption of such a system makes the importation of acids independent of the exigencies of the mixing process. It also tends to insure steady feed to the mixing plant, independent of importation difficulties, and does much to simplify the actual mixing operations.

Materials for Handling Raw and Mixed Acids.

It is advisable to use lead vessels and pipe lines for sulphuric acids up to 94 per cent. H_2SO_4, nitric acids of 85 per cent. HNO_3 and over, and mixed acids containing more than 20 per cent. H_2O.

With more highly concentrated sulphuric acids, oleums, and mixed acids containing not more than 20 per cent. H_2O mild steel should be substituted for lead, whilst earthenware is the best material for nitric acids of less than 85 per cent. HNO_3.

Actual Mixing.

It is not designed to give an exhaustive treatment of the preparation of mixed acids for all purposes, but in general the principles and practice of mixing to be outlined are of universal application. The actual mixing process may be carried out by simply running regulated supplies of the constituent acids through a vessel filled with a previously made mixture and containing a suitable cooling coil, or the acids may be run together through a coil immersed in cold water. More certain mixing is obtained by introducing the acids into a vessel provided with suitable agitating gear and cooling by an immersed cooling coil.

Nitro-Glycerine Mixed Acid—COMPOSITION.—A suitable mixed acid for nitrating glycerine has the following composition:—

	H_2SO_4	58.5 per cent.
HNO_2 content to be not more than 0.6 per cent.	T.N.A.	40.4 ,,
	H_2O	1.1 ,,

Owing to the very low water content of this mixture the acids used in its preparation must be highly concentrated.

NITRIC ACID. — Nitric acid manufacturing plants can produce an acid of 92 per cent. HNO_3 content quite easily, and this acid is suitable for making nitro-glycerine mixed acid.

SULPHURIC ACID. — Assume the nitric acid available contains 92 per cent. T.N.A.

For 100 tons of mixed acid containing 40.4 per cent. T.N.A., the weight of 92 per cent. nitric acid required is . . . $\frac{40.4}{92} = 43.9$ tons.

Thus the weight of sulphuric acid it is possible to add is $100 - 43.9 = 56.1$,,

And this weight of sulphuric acid must contain . . . . 58.5 ,, H_2SO_4.

Therefore the strength of the sulphuric acid must be . . $\frac{58.5}{56.1} = 104.3$ per cent. H_2SO_4.

This is fuming sulphuric acid or oleum.

OLEUM.—An oleum convenient to produce and handle contains 20 per cent. free SO_3 (known as 20 per cent. oleum) and analyses 104·5 per cent. H_2SO_4.

$$H_2SO_4 = H_2O + SO_3$$
$$98 = 18 + 80,$$

i.e., in H_2SO_4, 80 parts by weight of SO_3 are combined with 18 parts by weight of H_2O.

100 tons of 20 per cent. oleum = 80 tons H_2SO_4 + 20 tons SO_3,

This 20 tons SO_3 will combine with 4·5 tons H_2O to give 24·5 tons H_2SO_4.

therefore 100 tons 20 per cent. oleum = 104.5 tons H_2SO_4.

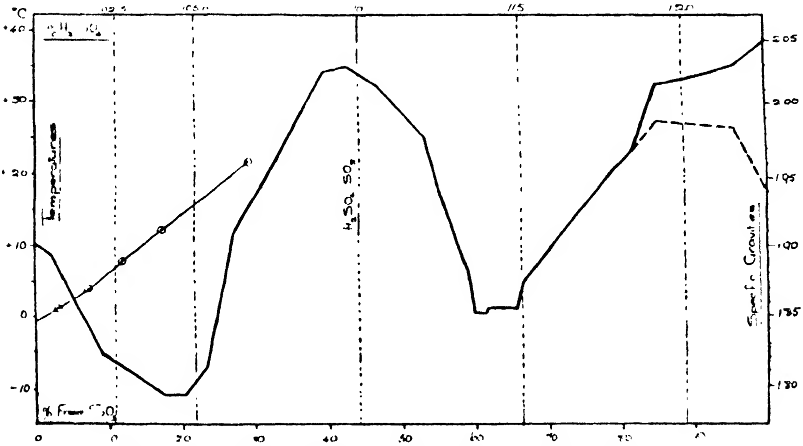

FIG. 107.—Melting Points and Specific Gravities of Oleum.

Melting-Points of Oleum.—An important point to bear in mind in selecting an oleum for mixing purposes is the melting-point. It would be most inconvenient to handle a highly fuming acid at temperatures higher than those ordinarily prevailing, and many difficulties would be experienced if frozen acid had to be dealt with. From the accompanying curve (Fig. 107), due to Knietsch, it may be seen that oleum containing about 20 per cent. free SO_3 is most suitable to work with having regard to the melting-point, as it remains liquid at all ordinary temperatures. A stronger acid which is liquid in summer contains 60 to 65 per cent. free SO_3.

THE PLANT.—Considerable heat is developed in mixing oleum and nitric acid, and, unless provision is made for cooling, rapid destruction of the mixing vessel may result. To get adequate cooling, to guard against excessive loss should control of the mixing get out of hand, and for more convenient working it is found advisable to mix in two stages.

In the first place the raw acids are mixed in preliminary mixing tanks, and finally a number of such mixes are blended together in blending tanks.

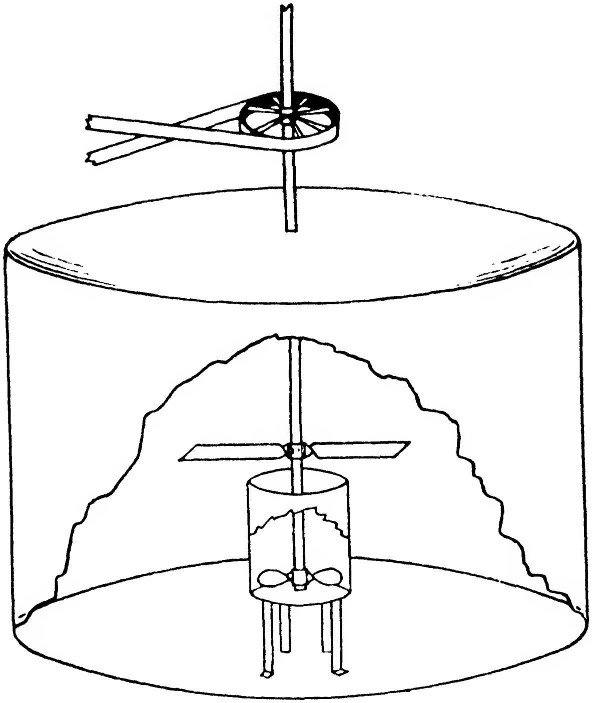

FIG. 108.—Stirring Device for Mixing Tank.

Preliminary Mixer.—This may be a lead, lead-lined steel, or mild steel tank of necessary capacity. Steel tanks are recommended for Nitro-glycerine Mixed Acid.

ADDITION OF ACIDS.—The procedure to be adopted in running in the various acids necessarily depends on the material of the tank, bearing in mind that oleum has considerable action on lead, whereas strong nitric acid has little effect, and that strong nitric acid rapidly attacks steel whilst oleum has little action.

AGITATION.—It is very important to have means for rapidly and efficiently mixing the acids. Although air agitation is often resorted to it is not advisable, since its use entails considerable formation of nitric acid fume, with consequent destruction of apparatus and loss of acid. Mechanically propelled agitating gear is to be preferred. It should be noted here that a mere swirling round and round of nitric and sulphuric acids does not bring about rapid or effective mixing. A stirring apparatus which is very suitable consists of a propeller fixed on a vertical shaft, suspended within an open lead or steel cylinder supported on legs which are bolted to the bottom of the mixing tank (see Fig. 108). Above the level of this cylinder and on the same shaft as the propeller is fixed a disrupter. When the inside cylinder is covered with liquid, revolution of the propeller causes a lifting of the liquid within the cylinder in addition to imparting a general rotary motion to the liquid. As the lifted liquid falls over the cylinder into the body of the tank, the revolving arms of the disrupter break the orderly flow and encourage mixing. To ensure rapid mixing the total height of the cylinder should not be more than is covered by the usual amount of the first acid introduced to the mixer.

COOLING.—As already noted the mixing of nitric acid and oleum causes considerable evolution of heat and tends to have a very destructive effect on the mixing apparatus. To minimise this effect, cooling must be brought about as rapidly as possible. This is done in a variety of ways, by the use of internally situated closed coils carrying cooling water, by external water jackets, by externally applied water sprays, or by combinations of these methods.

An effective way of ensuring sufficient cooling is to leave a supply of mixed acid in the mixer at the end of each mixing operation. This is thoroughly cooled before fresh acids are added, and the rise of temperature is now much less marked. The curves overleaf serve to illustrate the advantage of this procedure. The temperature of mixing should be watched by having a long-stemmed thermometer enclosed in a perforated steel tube immersed in the mixture.

Fume.—During mixing a considerable amount of fume is evolved, consisting chiefly of nitric acid with small proportions of oxides of nitrogen and nitrosyl-chloride. For this reason it is advisable to provide the mixing vessel with a close-fitting lid, and to see that all entry pipes, etc., are suitably luted. In order to preserve as pure an atmosphere as possible in the house where mixing is carried on, means should be provided

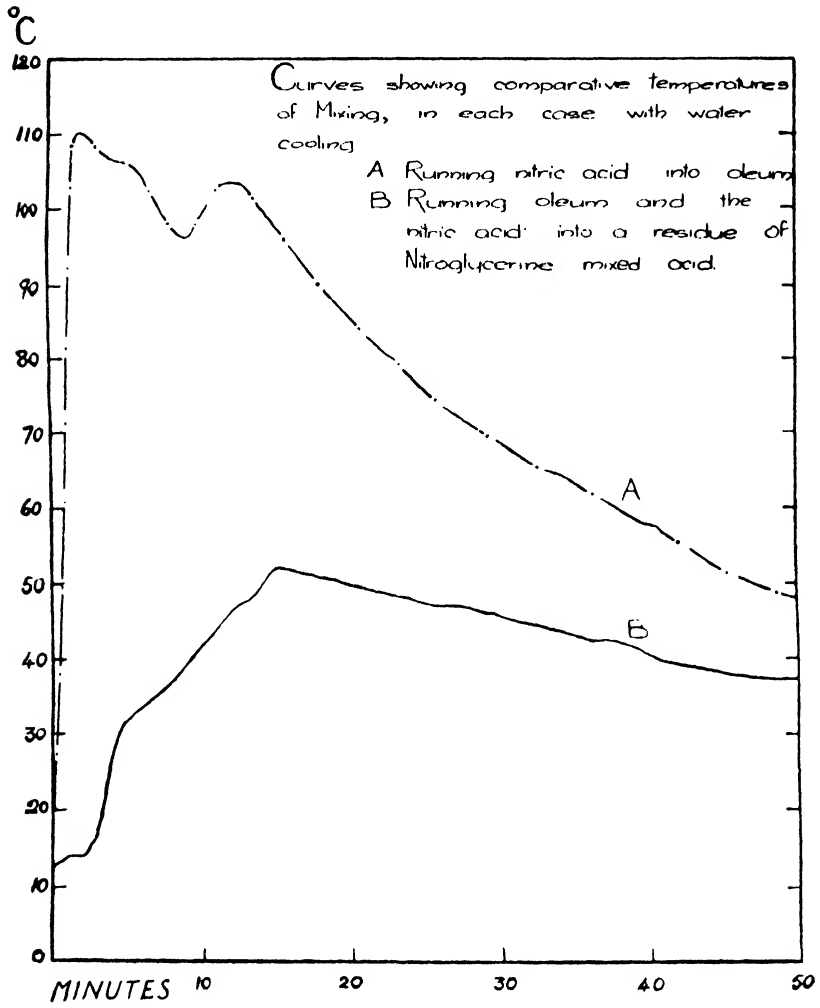

Fig. 109.

for exhausting the fumes from the mixer by causing an induced draught therefrom to a suitable chimney. To avoid waste of acid and to prevent undue pollution of the atmosphere, it is very desirable that the exhausted fume should be trapped in some absorption apparatus before discharging to the air.

Such an apparatus may consist of earthenware drain pipes packed with broken quartz, down which a constant stream of water, or weak nitric acid can be supplied through the agency of a Pohle lift. After sufficient circulation the weak acid so produced can be run out and utilised.

A sample of fume trapped in a glass vessel surrounded by ice from a mixing plant preparing nitro-glycerine mixed acid had the following composition:—

HNO_3 = 79 per cent.
H_2SO_4 and HCl = 1 „
H_2O = 20 „

Samples of nitric acid recovered in a small absorption tower on the same plant had the following compositions:—

Sample No.	Specific Gravity.	Per cent. HNO_3.	Per cent. H_2SO_4.	Per cent. HCl.
1	1·429	72·28	0·1	trace
2	1·417	68·70	0·5	„
3	1·398	63·40	0·3	„

Delivery of Mixed Acid to Blender.—When a mix is completed it is transferred to a blending tank by gravity, by means of pumps, or by use of compressed air. If by the latter, it is first run by gravity into an acid egg suitably situated.

Blending.—In the blend tank several mixes are collected and agitated by mechanical stirrers to get a uniform mixture.

Sampling.—Before a sample is removed for analysis it should be certain that thorough mixing has been effected and that the sample removed represents a uniform mixed acid. Too much attention cannot be given to sampling, as it is highly essential that the analytical result shall correctly represent the acid which is to be used for nitration purposes. If the analytical result recorded agrees with specification the

blend may be used for nitration.[1] If not, its strength has to be adjusted. It is "doped."

DOPING.—A certain latitude is allowed in the specification of a mixed acid. In the example already chosen, the specification reads:—

H_2SO_4 . . .	58.5 ± 0.4 per cent.
T.N.A. . . .	40.4 ± 0.4 ,,
H_2O	1.1 ± 0.4 ,,

Any blend of acid coming outside these limits needs a correcting mix or dope.

Successful doping depends on—
(*a*) Reliable sampling.
(*b*) Reliable analysis.
(*c*) Correct measurement of the dip of the blend to calculate its tonnage.
(*d*) Correct measurements for the ingredients of the dope, and correct analyses of these ingredients.

Type of Dope.—If doping is necessary, it is advisable that the correction be applied in as simple a manner as possible.

If one constituent can be used, *e.g.*, sulphuric acid,
(*a*) The acid can be added directly to the blender without the use of the preliminary mixer.
(*b*) Possible complications due to analysis of a mixed acid are avoided.

As a matter of practice blends are best prepared therefore with the HNO_3 content on the high side and the H_2SO_4 content on the low side of specification.

The water content or *dilution* of the blend will now determine what can be used for doping purposes:—

(i) If the dilution is high a strong dope is required, hence oleum is used. If oleum does not bring the blend within specification, a special method has to be worked out.
(ii) If the dilution is about normal, it is necessary to add an acid of about 1 per cent. dilution, *i.e.*, a mixture of 93 per cent. S.A. (7 per cent. dilution) and oleum (−4·5 per cent. dilution).

---

[1] For analysis, see p. 313.

(iii) If the dilution is low, 93 per cent. S.A. is added if this brings the resulting blend within specification; if not, water has to be introduced. The introduction of water is conveniently made by using nitric acids containing water.

Calculation of the Tonnage of a Sulphuric Acid Dope.

CASE I.—*High dilution* and use of oleum.

(i) (*a*) Let the analysis of the blend be

H_2SO_4	58.0 per cent.
T.N.A.	40.8 ,,
H_2O	1.2 ,,

and specification

H_2SO_4 . . .	58.5 ± 0.4 per cent.
T.N.A. . . .	40.4 ± 0.4 ,,
H_2O . . .	1.1 ± 0.4 ,,

(*b*) Suppose the tonnage of the blend be 150 tons.

(*c*) Let W = tonnage of the dope.

The T.N.A. content of the blend is 150×0.408 tons.

,, ,, ,, final blend is to be $(150+W) \times 0.404$ tons.

Since no T.N.A. is to be added in the dope, these two are equal,

$$\begin{aligned} \textit{i.e.} \quad (150+W)\,0.404 &= 150 \times 0.408 \\ \text{and} \quad 60.6 + 0.404\,W &= 61.2 \\ \therefore \quad W &= \underline{1.5 \text{ ton approx.}} \end{aligned}$$

When this is added the final analysis is calculated thus:—

$$\begin{aligned} \text{Present } H_2SO_4 \text{ content} = 150 \times 0.58 &= 87.0 \text{ tons} \\ H_2SO_4 \text{ added} = 1.5 \times 1.045 &= \underline{1.6} \;\;,, \\ \text{Total} \quad . \quad . &= \underline{\underline{88.6}} \;\;,, \end{aligned}$$

$$\therefore\ H_2SO_4 \text{ content} = \frac{88.6 \times 100}{151.5} = 58.5 \text{ per cent.}$$

$$\text{T.N.A.} \quad ,, \quad = \frac{150 \times 0.408 \times 100}{151.5} = 40.4 \text{ per cent.}$$

$$H_2O \quad ,, \quad = 1.1 \quad ,,$$

These are the specification figures.

The calculated composition may not come out so close as this case, but as long as it comes within ± 0·3 of specification on each constituent it is safe to apply the dope.

The 0·1 per cent. difference is allowed for slight variations in working.

(ii) Let the analysis of the blend be

H_2SO_4 = 57.6 per cent.
T.N.A. = 40.8 „
H_2O = 1.6 „

In this case the dilution is above the upper limit and the oleum dope will have to bring it down as much as possible to pass the blend. Hence it is desirable to add the *maximum* amount of oleum. For this purpose the T.N.A. content should be reckoned at its lowest safe limit, *i.e.*, 40·1 per cent. (allowing the 0·1 per cent. for variations in working).

Calculating T.N.A. to 40·1 per cent.

Equating T.N.A. in the doped and undoped blends.

$$(150 + W) \times 0.401 = 150 \times 0.408$$
$$\therefore \quad W = 2.62 \text{ tons.}$$

Calculated composition—

$$H_2SO_4 = \frac{(150 \times 0.576 + 2.62 \times 1.045) \times 100}{152.62} = 58.41$$

$$\text{T.N.A} = \frac{150 \times 0.408 \times 100}{152.62} = 40.1$$

$$H_2O = 1.49.$$

The method of working to limits is extremely valuable in cases of high dilution.

Case II.—Consider a blend of 150 tons of composition

H_2SO_4 = 59.0 per cent.
T.N.A. = 41.0 „
H_2O = 0.0 „

Suppose a 16-ton dope is made.

Then the final blend will contain 166 tons.

Present H_2SO_4 content = 150×0.59 = 88.5 tons
„ T.N.A. „ = 150×0.41 = 61.5 „
Final desired H_2SO_4 content = 166×0.585 = 97.11 tons
„ „ T.N.A. „ = 166×0.404 = 67.06 „
∴ H_2SO_4 to be added = 8.61 tons
and T.N.A. „ = 5·56 „

$$\therefore \quad 93 \text{ per cent. S.A. required} = \frac{8.61}{0.93} = 9.25 \text{ tons}$$

and N.A. required = $16 - 9.25$ = 6.75 tons.

Nitric acids available—

S.N.A. . . . 92 per cent. T.N.A.
W.N.A. . . . 64 ,, ,,

Let x = weight of S.N.A. required
Then $(6.75 - x)$ = weight of W.N.A. required.

Equating T.N.A. we get—

$$0.92x + (6.75 - x) \times 0.64 = 5.56$$
$$\therefore \quad 0.28x = 1.24$$
$$\text{and} \quad x = \underline{4.43 \text{ tons}}$$
$$\therefore \quad \text{wt. of W.N.A} = 6.75 - 4.43 = 2.32 \text{ tons.}$$

Thus the required dope is—

S.A. = 9.25 tons
S.N.A. = 4.43 ,,
W.N.A = 2.32 ,,
Total = 16.00 ,,

General Scheme.—The following table gives a general idea of the possibilities of normal doping :—

Dilution.	Dope required.
Up to 0·4 per cent. H_2O . .	Sulphuric acid, strong and weak nitric acids.
,, 0·4 to 0·6 per cent. H_2O .	Oleum, sulphuric acid, strong nitric acid.
,, 0·6 ,, 0·9 ,, ,, .	Sulphuric acid.
,, 0·9 ,, 1·2 ,, ,, .	Sulphuric acid and oleum.
,, 1·2 ,, 1·6 ,, ,, .	Oleum.

High Dilution.—High dilution may result from one or all of the following :—

(*a*) Water leaking into the acid through the holing of a cooling coil.
(*b*) Use of nitric acid of less than 92 per cent. T.N.A.
(*c*) Careless pumping (*e.g.*, a weaker mix being pumped as part of a blend of N.G. mixed acid by mistake).

With dilution exceeding 1·6 per cent., it will be necessary to arrange for supplies of more concentrated oleum or nitric acid in order to bring the blend within specification.

STORING.—The blend tanks may provide ample storage capacity, or it may be deemed advisable to transfer the blended specification acid from these to storage tanks *en route* for the nitration process. The storage capacity should be as ample as possible to relieve the mixing plant of undue worries as regards output, and to ensure availabiltiy of supplies to the mixed acid using plants. Further, it should be possible to transfer acid readily, *e.g.*, by pumping, from any storage tank to any other, so that should a leak develop, the acid may be pumped to safety.

PUMPING.—If pumping is necessary it is important to bear in mind that the maintenance of efficiency in the pumping units is vital for the proper working of the mixing plant. They must always be capable of handling the mixed acids. Centrifugal pumps made of steel or of cast iron handle mixed acids satisfactorily. The positive action type of pump, of which type the "Douglas" pump has found great use in pumping mixed acids, is very effective in doing heavy work against big heads.

Mixed Acid Suitable for Distillation. — OBJECT OF PROCESS.—It has been noted that only strong nitric acid may be used for nitro-glycerine mixed acid. In producing this strong nitric acid a certain amount of weak acid (55 per cent. to 70 per cent.) is produced,

(*a*) In the distillation.
(*b*) In the absorption towers.

In certain circumstances it may be desired to convert this acid to strong nitric acid.

THEORY.—The acid is mixed with concentrated sulphuric acid, which has a great affinity for water. Thus the process simply amounts to:—

Weak Nitric Acid + Concentrated Sulphuric Acid
= Strong Nitric Acid + Weak Sulphuric Acid.

The weak sulphuric acid produced is sent to the concentrators, where the excess water is driven off and concentrated sulphuric acid again produced.

AMOUNT OF WATER "RETAINED" BY SULPHURIC ACID.—Assume we have 100 tons of 94 per cent. sulphuric acid.

The residual sulphuric acid after distillation is to be 80 per cent. strength.

Let x be the water held back.

Then we have $(100 + x)$ tons of residual acid at 80 per cent.

Hence equating H_2SO_4 we get—

$$\begin{aligned} 100 \times 0.94 &= (100 + x) \times 0.8 \\ \text{i.e. } 94 &= 80 + 0.8x \\ . \quad x &= 17.5 \text{ tons.} \end{aligned}$$

With other strengths of sulphuric acid the following results are obtained (per 100 parts by weight):—

Concentration.	Water held back.
92 per cent.	15·0
93 „	16·2
94 „	17·5
95 „	18·8
96 „	20·0

CALCULATION OF MIXES.—It is clear that the amount of weak nitric acid in a mix (if the tonnage of sulphuric acid is fixed) will be solely dependent upon its concentration, and therefore the composition of the mixed acid will vary.

Supposing we have 100 tons of nitric acid at 61 per cent., which is to be distilled at a strength of 91 per cent.,

$$\text{the nitric acid produced} = \frac{61}{0.91} = 67 \text{ tons.}$$

$\therefore$ Water to be held back by sulphuric acid is 100 − 67 = 33 tons.

If the sulphuric acid be of 93 per cent. concentration, then 16·2 tons of water are held back by 100 of sulphuric acid.

$$\text{Hence 33 tons of water are held back by } \frac{100 \times 33}{16.2} = 204 \text{ tons.}$$

Hence sulphuric acid required = 204 „

Similarly using 94 per cent. sulphuric acid, amount required = 189 tons.

and „ 92 „ „ „ = 220 „

VARYING COMPOSITION OF MIXES.—In actual practice the concentration of the sulphuric acid is usually fixed. Assume this to be 94 per cent.

(*a*) Consider weak nitric acid of 54 per cent. strength.

$$100 \text{ tons W.N.A. produce } \frac{100 \times 54}{91} \text{ tons of strong acid} = 59 \text{ tons}$$

$\therefore$ water to be held back = 41 tons

$$\therefore \text{ sulphuric acid required} = \frac{100 \times 41}{17.5} = 234 \text{ tons.}$$

Thus the mixture consists of:—

	T.N.A.	H_2SO_4.	H_2O.
100 tons W.N.A.	54	...	46
234 „ sulphuric acid	...	220	14
334 „ mixed acid	54	220	50
Percentage composition	16·2 per cent.	65·8 per cent.	18·0 per cent.

(*b*) Considering weak nitric acid of 68 per cent. strength. We get by a similar calculation a mixture consisting of:—

	T.N.A.	H_2SO_4.	H_2O.
100 tons W.N.A. . .	68	...	32
149 " sulphuric acid .	...	140	9
249 " mixed acid . .	68	140	41
Percentage Composition .	27·3 per cent.	56·2 per cent.	16·5 per cent.

As these are the limits of acids usually produced in practice, mixes vary between these compositions. It will be noted that even the weaker mixed acid contains less than 20 per cent. of water and therefore such mixed acid may safely be stored in mild steel vessels.

THE MIXING.—Weak mixes are best made in lead or lead-lined mixers with lead cooling coils, owing to the very rapid action of weak nitric acid on mild steel.

Mixed Acid for Nitro-Cotton.—The "spent" acid resulting from the process of cotton nitration can be used as a basis in the preparation of fresh nitrating acid, only requiring to be strengthened to the required specification by the addition of concentrated raw acids.

The mixed acid used for the nitration varies according to the nitrogen content of the nitrated product. A mixed acid which has been largely used in the production of a nitro-cotton having a nitrogen content of 11·2 per cent. has the following composition:—

H_2SO_4 = 62.15 per cent. ± 0.3 per cent.
T.N.A. = 2.300 " ± 0 3 "
H_2O = 14.85 " ± 0.1 "

After nitration the diluted acid resulting—usually termed "spent" acid or "refuse" acid—has approximately the composition:—

H_2SO_4 = 61.0 per cent.
T.N.A. = 19.7 "
H_2O = 19.3 "

It is found convenient in practice to bring this "spent" acid up to specification by adding to it a quantity of a specially prepared concentrated mixture of sulphuric acid and nitric acids, usually called revivifying acid (R.V.A.).

Revivification.—As the spent acid is subject to variation in composition, it is not usually possible to bring about the adjustment of its composition just by the addition of a bulk of R.V.A., and for this reason it is a good plan to keep the R.V.A. mixture slightly low in H_2SO_4 content and add sulphuric acid finally for exact adjustment.

Revivification, therefore, may be expressed by the following equation:—

Spent Acid + R.V.A. + Sulphuric Acid = Nitro-Cotton Mixed Acid.

The spent acid produced in nitration has approximately the same volume as the mixed acid used. Thus, if the whole of the spent acid were revivified the mixed acid produced would be of ever-increasing bulk. For this reason a portion of the spent acid is usually distilled for the recovery of its constituent acids.

The proportions of spent acid and R.V.A. used for revivification depend upon their relative strengths. As the spent acid is of fairly constant composition, the amount of R.V.A. used in revivification will depend on its strength, and therefore the proportion of the spent acid produced in nitration which is made available for distillation is directly dependent on the strength of the R.V.A. Many factors may influence the strength of the R.V.A., and it has to be adjusted to suit the varying conditions of acid stocks, etc., on the acids area (see acids and water balance, p. 427).

PREPARATION OF R.V.A.—*Mixing.*—R.V.A. is conveniently prepared in steel tanks provided with steel cooling coils, since the acid is concentrated and oleum enters largely into its composition.

The acids which may be available for R.V.A. production are:—

1. Oleum	104·5	per cent.	H_2SO_4.
2. Sulphuric Acid	93·0	,,	,,
3. Strong Nitric Acid from Retorts	92·0	,,	T.N.A.
4. Weak ,, ,, ,,	64·0	,,	,,
5. Average ,, ,, Stills	85·0	,,	,,

In mixing oleum, sulphuric acid, strong nitric acid, and weak nitric acid in a steel tank, the acids are introduced in the order named.

Blending.—Individual mixes are blended as already described under the preparation of nitro-glycerine mixed acid. It is convenient to have the R.V.A. blending tanks elevated so that the R.V.A. can be run by gravity into the tanks used for preparing the nitro-cotton mixed acid.

Analysis.—Each blend of R.V.A. is sampled and analysed, and if its composition is not suitable, is doped, but this is rarely necessary.

Spent Acid Storage.—Spent acids of less than 20 per cent. water content may be stored in steel vessels, but if the dilution is higher, lead-lined vessels should be used. It is advisable to provide a perforated pipe for air agitation should an occasional stirring of the contents become desirable, *e.g.*, should a portion of very weak acid be added to the tank. For convenience of working the spent acid store tanks should be elevated. Separate delivery lines may lead to the nitro-cotton mixed acid blending tanks, and to pumps or acid eggs for delivery to the distillation plant.

THE PROCESS OF REVIVIFICATION.—First the amount of spent acid which can be dealt with is run into a steel blending tank provided with stirring gear. This is mixed until of uniform composition and then analysed. An accurate dip is now taken and the tonnage calculated. Knowing the composition of the spent acid and its tonnage, and knowing the composition of the R.V.A. and sulphuric acid available, a calculation is made to determine the amounts of the latter to be run into the spent acid to bring the whole to the desired composition. When everything is in, the blend is stirred until of uniform composition, sampled and analysed. As the water content of specification acid can only vary 0·1 per cent., the success of blending depends on strict accuracy in all dipping, and on the utmost care in sampling and analysis.

Occasionally the blend will require "doping."

CALCULATIONS.—Many methods, arithmetic, algebraic and graphic, have been developed for adjustment of mixed acids to specified compositions, and the actual method employed by any worker is often necessarily adapted to the particular conditions with which he has to deal.

For purposes of illustration, it is proposed to give examples of each of the above methods.

Assume the following analyses:—

	R.V.A.	Spent Acid.	Sulphuric Acid.	Mixed Acid.
H_2SO_4	60·0	61·0	93·0	62·15
HNO_3	34·0	19·7	...	23·00
H_2O	6·0	19·3	7·0	14·85
	100·0	100·0	100·0	100·00

The Arithmetic Method.—The principle involved is:—

1. To express the sulphuric acid and R.V.A. as 100 per cent. acids—thus eliminating all water from all *added* acids.
2. To express the composition of the spent acid available, and the mixed acid desired *under the same conditions.*

Now if the water content so found of the spent acid be B per cent., and that of the mixed acid be A per cent., then, since no water is added, the ratio $\frac{\text{spent}}{\text{mixed}}$ must be $\frac{A}{B}$, by the ordinary law of mixtures. An example will illustrate the method.

Consider the R.V.A.

If 100 per cent. H_2SO_4 had been used in its composition instead of the 93 per cent. acid available, the H_2SO_4 content would have been:—

$$\frac{100}{93} \text{ of } 60 = 64.52 \text{ per cent.}$$

$$\frac{100}{93} \text{ is the water elimination factor for T.N.A.}$$

For total elimination of water, the T.N.A. content must increase from 34 per cent. to 35.48 per cent.

$$\therefore \frac{35{\cdot}48}{34} \text{ is the water elimination factor for } H_2SO_4.$$

The spent and mixed acids must be treated similarly.

The spent acid, therefore, becomes:—

$$H_2SO_4 = \frac{100}{93} \text{ of } 61 = 65.58 \text{ per cent.}$$

$$\text{T.N.A.} = \frac{35.48}{34} \text{ of } 19.7 = 20.56 \quad ,,$$

$$\text{and } H_2O \text{ (by difference)} = 13.86 \quad ,, \quad . \; . \; . \; (B).$$

The mixed acid becomes:—

$$H_2SO_4 = \frac{100}{93} \text{ of } 62.15 = 66.82 \quad ,,$$

$$\text{T.N.A.} = \frac{35.48}{34} \text{ of } 23.0 = 24.00 \quad ,,$$

$$\text{and } H_2O \text{ (by difference)} = 9.18 \quad ,, \quad . \; . \; . \; (A).$$

Thus the percentage of spent acid in the mix

$$= \frac{100\,A}{B}$$

$$= \frac{100 \times 9.18}{13.86}$$

$$= 66.22 \text{ per cent.} \quad . \; . \; . \; (C).$$

But the T.N.A. in 100 parts of mixed acid

$$= 23.0 \text{ per cent.}$$

And the T.N.A. supplied by 66.22 (C) parts of spent acid

$$= \frac{66.22 \times 19.7}{100} = 13.05 \text{ per cent.}$$

∴ T.N.A. to be supplied by R.V.A. = 9.95 ,, . . . (D).

But R.V.A. contains 34 per cent. (E) HNO_3

$$\therefore \text{per cent. of R.V.A. in mix} = \frac{D}{E} = \frac{9.95}{34} \times 100 = 29.26 \text{ per cent.}$$

And spent in mix = 66.22 ,,

∴ S.A. (by difference) = 4.52 ,,

Thus supposing we have 110 tons of spent acid

$$\text{The total blend} = \frac{110}{0.6622} = 166.2 \text{ tons}$$

$$\therefore \text{ R.V.A. required} = 166.2 \times 0.2926 = 48.61 \text{ tons}$$

$$\text{and S.A.} \quad ,, \quad = 166.2 \times 0.0452 = 7.59 \quad ,,$$

For convenience and speed of working it is well to have a tabulated record book for this blending.

A convenient form is given on opposite page.

RECORD OF N.Co MIXING. BLEND No......

Analysis of:—

	R.V.A.	Spent.	S.A.	M.A.
H_2SO_4 . . .				
T.N.A. . . .				
H_2O . . .				
	100·0	100·0	100·0	100·0

Composition, as ...... % T.N.A.
and ...... % H_2SO_4, of:—

	R.V.A.	Spent.	M.A.
H_2SO_4 .			
T.N.A. .			
H_2O . .	Nil	(B)	(A)
	100·0	100·0	100·0

% Spent in Mix = $\frac{(A)}{(B)} \times 100$ = ... (C)

T.N.A. in 100 parts M.A. =

" in (C) " Spent =

" from R.V.A. = ...(D)

% R.V.A. in Mix = $\frac{(D)}{(E)}$ =

" S.A. " =

QUANTITIES REQUIRED.

	R.V.A.	Spent.	S.A.	Total.
Weight . .				(F)
Dip . .				

CALCULATED ANALYSIS.

	H_2SO_4.	T.N.A.
From R.V.A.		
" Spent .		
" S.A. .		
Total . .	(G)	(H)

ACTUAL ANALYSIS.

% $H_2SO_4 = \frac{(G)}{(F)}$ = ... H_2SO_4		
" T.N.A. = $\frac{(H)}{(F)}$ = ... T.N.A.		
" H_2O = ... H_2O		
100·0	100·0	100·0

DOPE.

	Weight.	Dip.
R.V.A.		
Spent .		
S.A. .		
Total .	(K)	

	H_2SO_4.	T.N.A.
From M.A.		
" Dope		
Total .	(L)	(M)

CALCULATED ANALYSIS.

% $H_2SO_4 = \frac{L}{F+K}$ = ...

" T.N.A. = $\frac{M}{F+K}$ = ...

" H_2O = ...

100·0

ACTUAL ANALYSIS.

H_2SO_4		
T.N.A.		
H_2O		
	100·0	100·0

Algebraic Method—

Let x = percentage of R.V.A. in mixed acid
" y = " spent acid "
Then $100 - (x + y)$ = " sulphuric acid "

Equating H_2SO_4 we get—

$$\text{(i.)} \quad \frac{60.0x}{100} + \frac{61.0y}{100} + 93 - \frac{93x}{100} - \frac{93y}{100} = 62.15$$

Equating HNO_3 we get—

$$\text{(ii.)} \quad \frac{34.0x}{100} + \frac{19.7y}{100} = 23$$

$$\begin{array}{lllll}
\text{(iii.)} & \text{(i.)} \times 100 & = & 60x + 61y + 9300 - 93x - 93y & = 6215 \\
\text{(iv.)} & \text{(iii.) collected} & = & 33x + 32y & = 3085 \\
\text{(v.)} & \text{(ii.)} \times 100 & = & 34x + 19.7y & = 2300 \\
\text{(vi.)} & \text{(iv.)} \div 32 & = & 1.031x + y & = 96.406 \\
\text{(vii.)} & \text{(v.)} \div 19.7 & = & 1.726x + y & = 116.751 \\
\text{(viii.)} & \text{(vii.)} - \text{(vi.)} & = & 0.695x & = 20.345 \\
 & \text{whence} & & x & = \underline{29.27} \\
 & \text{from (vii.)} & & y & = 116.751 - 50.52 \\
 & \therefore & & y & = \underline{\underline{66.23}}
\end{array}$$

Thus the required percentages are—

$$\left.\begin{array}{lcl}
\text{R.V.A.} & = & 29.27 \text{ per cent.} \\
\text{Spent acid} & = & 66.23 \quad " \\
\text{Sulphuric} \quad " & = & 4.50 \quad "
\end{array}\right\}$$

Graphic Method.—The method described below was developed by R. A. Fowler[1] at H.M. Factory, Gretna, and was used successfully at Gretna for many hundreds of revivifications. It can be used just as readily for doping.

Let the percentages of H_2SO_4 and HNO_3 in the nitrating acid be x and y respectively, in the spent acid x_1 and y_1, and in the revivifying acid x_2 and y_2, and the percentage of H_2SO_4 in the sulphuric acid x_3. These compositions may be shown in graphical form, plotting percentages of H_2SO_4 on abscissæ and of HNO_3 on ordinates.

For any given case x and y are both fixed quantities. Let the point (x, y), Fig. 111, be N, and the point $(x_3, 0)$ lying on the x-axis, V. If the points V and N be joined and this line produced indefinitely, the portion produced is the sulphuric acid line.

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1919, **88**, 34-36.

Now x_1, y_1, x_2, y_2 vary within certain limits according to plant working. Let the points (x_1, y_1) and (x_2, y_2) for any particular case be S and R respectively. Now the line SR will cut the line VN produced, for if not, revivification by means of the revivifying and sulphuric acids available is impossible (see below). Let P be the point of intersection.

(In what follows, an acid having a composition represented by the point S will be shortly called "S acid," and similarly for other points.)

It can be readily shown that by mixing S acid and R acid in suitable proportions, any acid of composition lying on the line SR may be made, and no other composition can be made by mixing S acid and R acid (see Fig. 110). For if x_2 be greater than x_1 the sulphuric acid content of any mixture of the two must be greater than x_1 and less than x_2, that is, it must lie between x_1 and x_2.

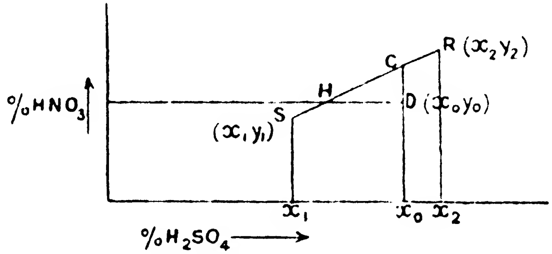

Fig. 110.

Similarly, the nitric acid content of any mixture of the two must lie between y_1 and y_2.

Let D be any point lying between x_1 and x_2 and also between y_1 and y_2 and let its co-ordinates be x_0 and y_0. To obtain an acid whose sulphuric content is x_0 (by the ordinary rule for mixtures) S acid is to be mixed with R acid in the ratio $(x_2-x_0) : (x_0-x_1)$. Similarly, to obtain an acid having a nitric acid content of y_0, S acid must be mixed with R acid in the ratio $(y_2-y_0) : (y_0-y_1)$. In order that both nitric and sulphuric acid contents may be satisfied $(x_2-x_0)/(x_0-x_1)$ must be equal to $(y_2-y_0)/(y_0-y_1)$. Let the ordinate x_0 cut RS at C and the ordinate y_0 cut it at H. Then $(x_2-x_0)/(x_0-x_1)$ $=$CR/CS, since the ordinates are parallel, and $(y_2-y_0)/(y_0-y_1)$

=HR/HS similarly. For $(x_2-x_0)/(x_0-x_1)$ to be equal to $(y_2-y_0)/(y_0-y_1)$, HR/HS must be equal to CR/CS, that is, C must coincide with H, and D must lie on SR. Therefore if R acid and S acid be mixed, the composition of the resulting blend lies on SR. Since P lies on SR (see Fig. 111), the acid represented by it may be made by mixing S acid and R acid in the proportion of the lengths of PR to PS. Similarly since N lies on PV, the acid represented by it (nitrating acid) may be made by mixing P acid and V acid in the proportions of the lengths of NV and NP.

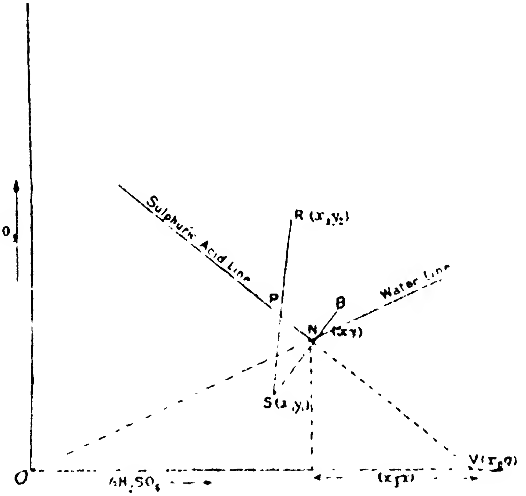

FIG. 111.

Now since both N and V are fixed points the length of NV is constant and equal to $\sqrt{y^2+(x_3-x)^2}$ and the tan. of the angle that NV makes with the x axis is $y \div (x_3-x)$.

Consider the case of a unit weight of P acid and suppose PN equal to VN $\div m$, then, in order to obtain N acid, V acid and P acid must be mixed in the proportion PN to VN, *i.e.*, $\frac{1}{m}$ of V acid to every unit of P acid, giving $\frac{m+1}{m}$ units of N acid. Therefore if the line VN produced be graduated towards P with divisions each equal to $\frac{1}{z}\sqrt{y^2+(x_3-x)^2}$, where

z is any convenient integer, each graduation will represent $\frac{1}{z}$ units of V acid to a unit of P acid.

Similarly, if ON be joined and produced it becomes the water line. It may be divided in the same manner as the sulphuric acid line into divisions each equal to $\frac{1}{z}\sqrt{x^2+y^2}$. The tan. of its angle is $\frac{y}{x}$. This may be found useful in extreme cases for blends in which the content of sulphuric and nitric acids is high, for in such cases the line joining B (the point representing the composition of the blend) to S may not cut the sulphuric acid line and the point P will then fall on the water line. This, however, should only happen in exceptional cases, as it is obviously bad practice to add water, if it can possibly be avoided, since it involves the introduction into the system of water which must be removed at a later stage.

Now for any particular composition of nitrating acid it is plainly not necessary to construct the whole of the graph as shown on the diagram. Only that portion need be drawn as shall contain the points N, S, and R (both S and R varying according to plant working), and this portion should be enlarged to a suitable size. The limits within which the composition of spent and revivifying acids vary in plant practice can readily be determined and the graph constructed accordingly. The highest nitric acid content in revivifying acid and the lowest in spent acid will fix the nitric acid limits, and similarly for the sulphuric acid content. The limits being fixed, the point N is found and from it in the direction of P a line is drawn making an angle having a tan. of $y/(x_3-x)$ with the x-axis and produced right across the graph. This line is divided into equal divisions from N towards P, each division being equal to $\sqrt{y^2+(x_3-x)^2}/1000$ units (or some convenient multiple of it). Then each division will represent 0·001 ton of sulphuric acid per ton of (revivifying + spent) acid. The graph is then complete.

The water line may be inserted if thought desirable. From N a line is drawn in the proper direction, as in the diagram, making an angle with the x-axis having a tan. of y/x, and is divided into equal divisions each equal to $\sqrt{x^2+y^2}/1000$ units (or some convenient multiple). Each division will represent 0·001 ton of water per ton of (revivifying + spent) acid.

The method of using the graph is simple. The compositions of the spent and revivifying acids to be used are plotted by means of two pins; a graduated ruler is placed close to these and the distances SP and RP are noted. Then tons of spent acid × SP/RP give tons of revivifying acid required. And (tons spent + tons revivifying acid) × reading on the sulphuric acid (or water) line give tons of sulphuric acid (or water) required.

When using the graph for adjusting the strength of blends that do not come up to specifications, the point B is plotted representing the composition of the blend. (*a*) If B falls on either the sulphuric acid or the water line the addition required is immediately read off, for tons of blend × reading gives tons of sulphuric acid or water required. (*b*) If B falls above the sulphuric acid (or water) line the blend may be mixed with spent acid in the same manner in which revivifications are made. (*c*) If B falls below the sulphuric acid (or water) line, revivifying acid may be used in the same manner in which revivifications are made.

Example.—It is required to construct a graph for the revivification of spent acid varying in composition between 19 and 21 per cent. HNO_3 and 60 and 62 per cent. H_2SO_4. The revivifying acid produced on the plant varies between 28 and 32 per cent. HNO_3 and 59 and 63 per cent. H_2SO_4. The nitrating acid is to be 62·15 per cent. H_2SO_4 and 23 per cent. HNO_3 and the sulphuric acid available contains 93 per cent. H_2SO_4. The limits of the graph are in this case 19 to 32 per cent. HNO_3 and 59 to 63 per cent. H_2SO_4, and therefore a scale of 1 in. to 1 per cent. will be convenient. The tan. of the angle that the sulphuric acid line makes with the x-axis $\frac{y}{x_3-x} = \frac{23}{93-62\cdot15} = \frac{23}{30\cdot85}$. The sulphuric acid line can then be drawn. If considered necessary the water line can be inserted as well. The tan. of its angle is $\frac{y}{x} = \frac{23}{62\cdot15}$. The divisions must now be marked off on the sulphuric acid line. Each is to be $\sqrt{y^2+(x_3-x)^2} \div 1000$ in., *i.e.*, approximately $\frac{1}{26}$ in. Consequently if divisions of $\frac{1}{13}$ in. be marked off they can be

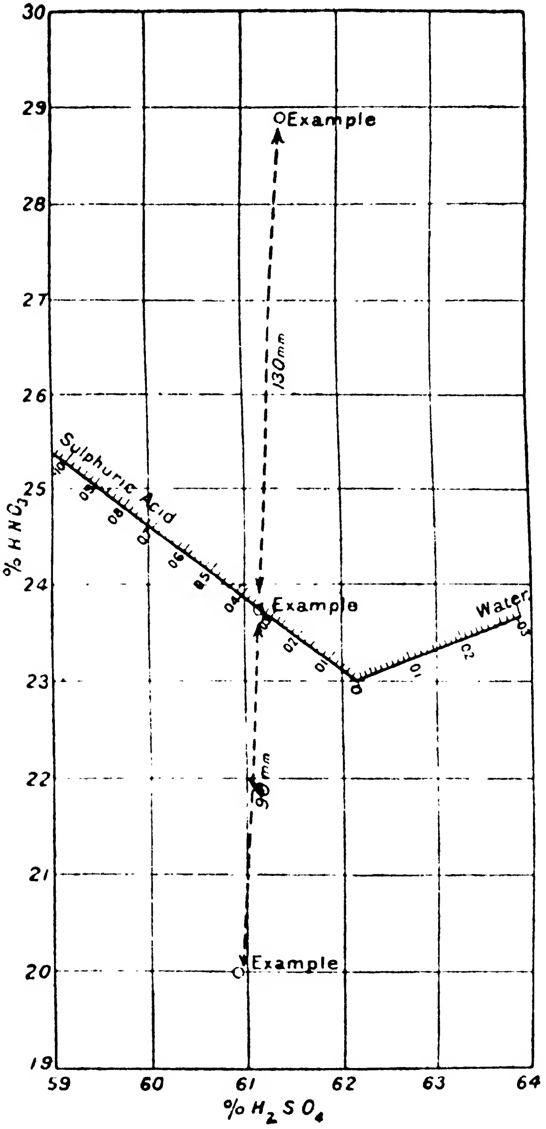
30
29
28
27
26
25
24
23
22
21
20
19
% HNO$_3$
59
60
61
62
63
64
% H$_2$SO$_4$
Example
130mm
Sulphuric Acid
Example
Water
90mm
Example

FIG. 112.

numbered 0·002, 0·004, 0·006, etc. The divisions on the water line are to be $\sqrt{x^2+y^2} \div 1000$, or nearly $\frac{1}{18}$ in.

An example of a revivification by the above graph is given. Spent acid 60·9 per cent. H_2SO_4, 20 per cent. HNO_3; revivifying acid 61·4 per cent. H_2SO_4, 28·9 per cent. HNO_3. The distance PS is 96 mm. and RS is 130 mm. The sulphuric acid reading is 0·034. Therefore 100 tons of spent acid will require $100 \times 96 \div 130 = 73{\cdot}85$ tons of revivifying acid, and the amount of sulphuric acid required will be $173{\cdot}85 \times 0{\cdot}034 = 5{\cdot}91$ tons. A reduced sketch of the above graph is given in Fig. 112.

In practice the graph is best mounted on a sheet of composition board strengthened with an edging of batten and is covered with tracing cloth to preserve it. When the pin-holes become too numerous the tracing cloth is renewed.

The graph is approximately 14 in. by 18 in., and any constituent can be readily calculated to within 0·02 per cent. in the nitrating acid.

General Formula.—L. Clément[1] gives the following general formulæ for revivifying spent acids after nitration :—

$$N = \frac{100\,[s\,(y-y^1) + xy^1 - x^1y]}{n\,(s-x) - ys}$$

$$S = \frac{100\,[n\,(x-x^1) + x^1y - xy^1]}{s\,(n-y) - nx}$$

Where N = weight of nitric acid per 100 parts by weight of spent acid
S = „ sulphuric „ „ „
x = per cent. H_2SO_4 in original mixed acid
y = „ HNO_3 „ „
x^1 = „ H_2SO_4 in spent acid
y^1 = „ HNO_3 „
s = strength of sulphuric acid used to revivify
n = „ nitric „ „

Modified Revivification Process.—A slightly modified procedure for the revivification of spent nitrating acids is outlined by W. Young[2] as follows :—

In the process of preparing the nitration mixtures, spent

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[1] *Le Caoutchouc et La Gutta-Percha*, 1907, **8**, 3019.

[2] *J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 315-16.

or refuse acid from the manufacture of nitro-cotton receives a preliminary adjustment by the addition of fuming nitric acid and oleum. This treatment corrects the composition of the refuse acid, bringing it somewhere near the composition specified for the nitration process. The corrected mixture, or "bulked acid," as it is called, may prove to fall within the limits allowed in the specification laid down for the nitrating mixture, but it may not do so and will therefore require further correction, which is effected by addition of nitric acid, oleum, or refuse acid, or usually of two of these acids, in calculated proportions. The use of water is avoided, except under special circumstances.

Algebraic Calculation.—The following algebraic method has been used for the calculation of the proportional parts at a large explosives factory with satisfactory results. After trial it has proved much less laborious than the arithmetical method and more adaptable to changing conditions than the graphical method, and with certain justifiable assumptions it can be used for constructing tables from which the proportional parts may be written down.

The method is most easily demonstrated by the working of examples, and, for the sake of convenience, the abbreviations N/A, S/A, R/A, M/A, and B/A will be used respectively for nitric acid, oleum, refuse acid, specified mixed acid, and the "bulked acid" referred to above.

Example 1.—A batch of bulked acid is found to require correction by means of 90 per cent. nitric acid and 20 per cent. oleum to bring it to a certain specified composition. Let the required proportions be 100 parts of bulked acid, x parts of oleum, and y parts of nitric acid, on mixing which $100+x+y$ parts of the specified mixed acid will be obtained. Two independent equations are available for finding the values of x and y. The example is worked out as follows:—

Acid.		B/A.	S/A.	N/A.	M/A.
Analysis	per cent. HNO_3 .	22·0	0·0	90·0	23·0
	" H_2SO_4 .	66·0	104·5	0·0	67·0
	" H_2O .	12·0	-4·5	10·0	10·0
		100·0	100·0	100·0	100·0

The equation connecting HNO_3 contents is:—

$$100 \times \frac{22.0}{100} + x \times \frac{0.0}{100} + y \times \frac{99}{100} = \frac{23\,(100 + x + y)}{100}$$

Rewritten, this equation becomes $- 23x + 67y = 100$

Similarly, the equation from H_2O contents becomes . . . . . $14.5x = 200$

Solving these equations, $x = 13{\cdot}793$ and $y = 6{\cdot}228$.

The required proportions are therefore 100 parts of bulked acid, 13·793 parts of oleum, and 6·228 parts of nitric acid.

Example 2.—A general case in which the correcting acids are refuse acid of known composition and 92 per cent. nitric acid. Proceeding as before, we have the following:—

Acid		B/A.	R/A.	N/A.	M/A.
Analysis	per cent. HNO_3 .	a	19·0	92·0	23·0
	„ H_2SO_4 .	b	68·0	0·0	67·0
	„ H_2O .	c	13·0	8·0	10·0
		100	100·0	100·0	100·0

The HNO_3 and the H_2O contents furnish two equations, viz.:—

$$4x - 69y = 100\,(a - 23) \quad . \; . \; . \; (1) \text{ connecting } HNO_3 \text{ contents,}$$

$$\text{and } 3x - 2y = 100\,(10 - c) \quad . \; . \; . \; (2) \text{ connecting } H_2O \text{ contents.}$$

Solving equations (1) and (2), we find—

$$x = 34.673\,(10 - c) - 1.005\,(a - 23),$$

$$\text{and } y = 2.010\,(10 - c) - 1.508\,(a - 23).$$

These general formulæ for x and y may now be used for drawing up tables, on the assumption that the compositions of the correcting acids and the specific mixed acid are constant. This assumption is dealt with later.

Construction of Tables:—

In practice the terms $(10 - c)$ and $(a - 23)$ are usually of small magnitude, and a working table from which the proportional parts of correcting acids can practically be read off is easily constructed.

The following skeleton table is drawn up for the conditions given in Example 2:—

TABLE I.

Parts of Correcting Acids per 100 *parts of Bulked Acid.*

Parts refuse acid = 34·673 (10 − c) − 1·005 (a − 23).
,, nitric ,, = 2·010 (10 − c) − 1·508 (a − 23).

10 − c or (a − 23) =	0·01	0·02	0·03	0·1	0·2	0·3	1·0	2·0
34·673 (10 − c) =	0·35	0·69	1·04	3·47	6·94	10·40	34·67	69·35
1·005 (a − 23) =	0·01	0·02	0·03	0·10	0·20	0·30	1·01	2·01
2·010 (10 − c) =	0·02	0·04	0·06	0·20	0·40	0·60	2·01	4·02
1·508 (a − 23) =	0·02	0·03	0·05	0·15	0·30	0·45	1·51	3·01

In Example 2, if $a = 22·65$ and $c = 9·85$, then $(a - 23) = -0·35$ and $(10 - c) = 0·15$. Using the formulæ or the completed table it will be found that 5·55 parts of refuse acid and 0·83 part of nitric acid are required to correct 100 parts of bulked acid.

Similar tables can be constructed for correction (1) with oleum and nitric acid, and (2) with oleum and refuse acid.

If in using any table or formula negative results are obtained, correction is impossible with the acids represented in the table, and must be carried out by some other combination of acids. For instance, in Example 2, if $a = 22·65$ and $c = 10·55$, oleum and nitric acid are required for correction, and Table I. would give a negative result.

The use of tables is possible on the assumption that the refuse acid, oleum, and nitric acid are constant as regards composition. In practice this is never the case, but variations within ± 2 per cent. of the average compositions have little effect, as is shown in Table II.:—

TABLE II.

1000 *lb. of Nitric Acid added to* 100,000 *lb. of Mixed Acid. Calculated Effect of a* 2 *per cent. Variation in the Strength of the Nitric Acid on the Composition of the Resulting Mixture.*

Composition of the original mixed acid.	Composition after addition of		Variations in resulting composition.
	1000 lb. of 90 N/A.	1000 lb. of 92 N/A.	
22·0 % HNO_3 68·0 ,, H_2SO_4 10·0 ,, H_2O	22·673 % HNO_3 67·327 ,, H_2SO_4 10·000 ,, H_2O	22·693 % HNO_3 67·327 ,, H_2SO_4 9·980 ,, H_2O	+ 0·020 % HNO_3 + 0·000 ,, H_2SO_4 0·020 ,, H_2O
100·0	100·000	100·000	0·000

The limitations of the method will be obvious to chemists employed in acid-control laboratories.

Graphical Treatment.—The algebraic calculation outlined above, due to W. Young, for correcting "bulked" acid to a mixed acid specification is treated graphically by R. A. Fowler.[1]

The composition of nitrating acid is fixed in the present case at HNO_3 23 per cent., H_2SO_4 67 per cent., H_2O 10 per cent., and may vary only within certain definite narrow limits.

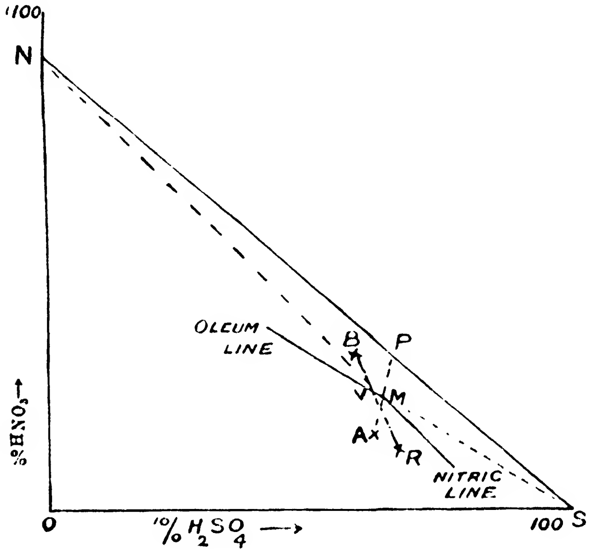

FIG. 113.

The composition of oleum (H_2SO_4 104·5 per cent.) and that of nitric acid (HNO_3 90 per cent.) are also fixed (with slight variations which do not greatly affect the calculation as explained in Young's article).

In Fig. 113 percentages of nitric acid are plotted on ordinates and percentages of sulphuric acid on abscissæ. If N represents the composition of the nitric acid available and S that of the oleum, the line NS shows the acids which can be produced by mixing N acid with S acid. If NS be divided into 100 equal parts the percentage of each constituent necessary for any definite composition represented by any

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 166-67.

point on the line may be read off. For example, if the divisions be numbered from 0 to 100 from S to N, then at any point in the line the percentage of nitric acid is indicated; suppose the reading be 72, then the acid represented by that point may be made by mixing 72 per cent. of nitric acid with 28 per cent. oleum.

The point representing the nitrating acid, M, does not lie on the NS line but nearer to the origin. Join NM and produce. Join SM and produce. Since the points N, M, and S are fixed, the lengths of NM and SM are constant and may be readily calculated. If, now, the part produced in each case be divided as from point M into equal parts each equal to one-hundredth of the lines NM and SM respectively, each division represents one-hundredth of a unit of nitric acid or oleum as the case may be (the divisions are omitted in Fig. 113 for clearness).

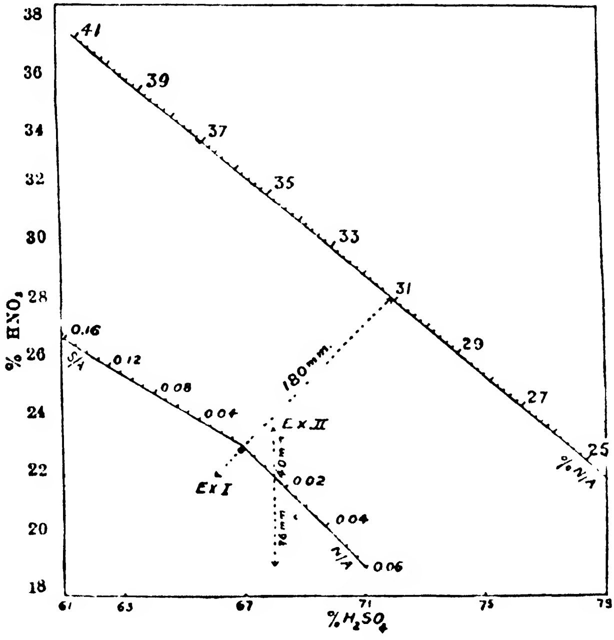

FIG. 114.

The graph is used as follows:—

Case 1.—The point representing the composition of the bulked acid falls on the origin side of both oleum and nitric lines (*e.g.*, at A). A rule is placed through A and M, cutting the line NS at P, and the distances AM and MP and the reading at P are noted. Then tons of bulked acid multiplied by AM/MP gives tons of adjusting acids required, of which P per cent. is nitric acid and the rest (100 − P per cent.) is oleum.

Case 2.—The point representing the composition of the bulked acid falls on the other side of the oleum and nitric lines (*e.g.*, at B). This may be adjusted by the use of refuse acid with nitric acid or oleum. When the points representing the bulked acid (B) and refuse acid (R) are joined, the line will cross either the nitric or oleum line, *e.g.*, at V. The distances BV and RV and the reading at V are noted. Then tons of bulked acid multiplied by BV/RV gives tons of refuse acid required. And (tons of bulked acid + tons of refuse acid) multiplied by reading at V gives tons nitric acid (or oleum) required.

Case 3.—The point representing the composition of the bulked acid falls on the nitric or oleum line. Then tons of bulked acid multiplied by the reading at the point gives tons of nitric acid (or oleum) required.

It is not necessary to draw the whole of the graph for practical working. That portion only round the point M need be drawn, say HNO_3 18 to 36 per cent. and H_2SO_4 62 to 74 per cent. (see Fig. 114). The higher limits are determined by the necessity for including a good part of line NS. The graph is prepared about 18 by 12 in., allowing 1 in. for 1 per cent. Plot the point M (67, 23). Calculation shows then the line NS passes through the points (62·7, 36) and (73·15, 27) and it may then be drawn. Divide this line between these two points into ten equal parts (each 1·379 in.) and continue the divisions the whole length of the line. The first of these two points represents an acid of composition 40 per cent. nitric acid and 60 per cent. oleum, and the second 30 per cent. nitric acid and 70 per cent. oleum; they may then be marked 40 and 30 respectively and the other divisions to correspond.

The oleum line may now be drawn from M in the right direction by means of the tan. of its angle with the abscissa 23/37·5 and divided into divisions each equal to $\frac{1}{100}\sqrt{23^2+37{\cdot}5^2}$

(=0·44 in. approx.). Similarly to the nitric line, the tan. of its angle being 67/67 and the divisions being equal to $\frac{1}{100}\sqrt{67^2+67^2}$ (=0·947 in. approx.).

Two examples are worked out with the aid of the graph.

Example 1.—Take 100 tons of bulked acid with composition 22 per cent. HNO_3 and 66 per cent. H_2SO_4. Then from the graph AM/MP is 36/180 and the reading at P is 31·1. Then acid required for adjustment is 100 × 36 ÷ 180, or 20 tons, of which 31·1 per cent. is HNO_3, *i.e.*, 6·22 tons of nitric acid and 13·78 tons of oleum. The calculated composition of the blend resulting from this mixture is HNO_3 22·998 per cent. and H_2SO_4 67·002 per cent.

Example 2.—Take 100 tons bulked acid with composition 23·6 per cent. HNO_3 and 68 per cent. H_2SO_4, and suppose the refuse acid available has composition 19 per cent. HNO_3 and 68 per cent. H_2SO_4. Then from the graph BV/VR is 40/76 and reading at V is 0·015. Tons of refuse acid required is 100 × 40 ÷ 76, *i.e.*, 52·6 tons. To this must be added 152·6 × 0·015, *i.e.*, 2·29 tons of nitric acid. The calculated composition of the blend resulting from this mixture is HNO_3 23·01 per cent., and H_2SO_4 66·99 per cent.

Should the composition of the nitrating acid be changed—a rare occurrence—a fresh graph would have to be constructed (this objection would apply equally to the tables used in connection with the algebraic method). The one graph covers all changing conditions in composition of refuse acid and small changes in composition of nitric acid and oleum.

STORING.—When a blend has passed specification it may conveniently be pumped or blown to steel store tanks. In calculating the storage requirements for mixing purposes it is advisable to make allowance for—

(1) Occasional doping; (2) a tank occasionally being out of commission for repairs.

PLANT WORKING.

The Avoidance of Trouble.

The following points are the result of considerable experience in the handling of large quantities of mixed acids:—

1. **Materials for Mixers and Coils.**—For making strong

mixes (up to 10 per cent. dilution) steel tanks with steel cooling coils are most serviceable.

For mixes from 10 per cent. to 20 per cent. dilution it is advisable to use lead-lined tanks fitted with lead cooling coils, since—

(1) There is very little heating effect, and consequently very little bulging of the lead.
(2) Lead is the better material in the presence of the weak acid used.

2. **Leaking Coils.**—A leaking coil is indicated by a rise in temperature. The water should be immediately shut off, and all running of acid stopped. If the mixer is fuming badly, probably due to the presence of weak acid, oleum or concentrated sulphuric acid should be run in. It is advantageous to have an external method of cooling. A 1-in. pipe perforated with holes running round the mixer about 2 in. from it, and held in position by brackets fitted to the lid, is suitable. The constant spray of water on the outside of the mixer cools down the acid in a reasonable time. The stirrer should be kept going until the acid is safe to pump.

Note.—Water control valves should be external to the mixing house, so that they can be handled if fuming is prevalent.

3. **Hot Lines.**—If a pump line becomes hot, it is probably an indication that nitric acid is leaking into the mixer and line (this is indicated in this manner only when mixers are pumped empty). Sufficient sulphuric acid or oleum should be run into the mixer to fill the lines and pumps; this will stop the corrosion.

4. **Seizing of Valves.**—A mixing plant is usually fitted with a large number of acid valves. To avoid the use of undue force in turning valves, which causes endless breakages, every valve should be regularly turned twice a day. The gland should not be tightened when the valve wants repacking, for tightening often causes seizing. In packing valves it is found that two turns of thin cord (blue asbestos cord soaked in boiling mineral jelly) are better than one turn of thick cord.

Care should be taken that the gland is never removed when there is a head of acid in the line to which it is connected, *otherwise the pressure will force out the plug and may cause a serious accident.* The line must first be carefully drained before removal of a gland.

5. **Cracked Castings.**—Cast steel is much less liable to crack than cast iron. Undue strain should be avoided in linking up and fixing.

6. **Air Locks.**—Air locks in lines delivering acids by gravity cause very slow running, or may stop the flow altogether. This may be avoided by having vertical pipes let into the lines at points where a slight rise or twist suggests the possibility of air being trapped. The height of the pipe must be above that of the maximum level of acid in the supplying vessel. If there is risk of bubbling and consequent splashing, it is necessary to have near the top of the air-release pipe a trap similar to that sketched in Fig. 115.

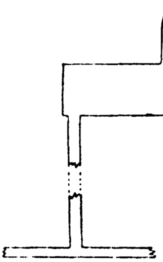

FIG. 115.
Air Release Trap.

7. **Corrosion of Tops of Tanks.**—Corrosion will occur

(1) At any place where there is a possible escape of fume (at joints for entry pipes, etc.); the remedy for this is obvious—to keep all joints tight.

(2) Round the dip hole, due to—

(*a*) Escape of fume.

(*b*) Drops of acid dripping from the dip rod.

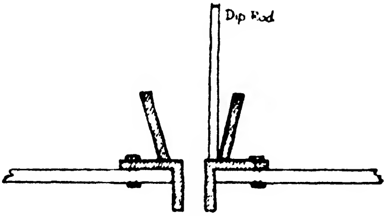

FIG. 116.

A small funnel-shaped casting covered with lead, or cast in regulus metal, with a space to carry the dip rod, is an efficient remedy. The lead or complete casting is easily replaced without damage to the tank, the casting being merely screwed to the lid of the tank.

8. **Acid in Mixers.**—It is good practice to leave mixed acid, oleum, or sulphuric acid in a steel mixer unless all entry lines are broken. Otherwise if nitric acid leaks in it will cause bad corrosion.

9. **Lubricants.**—Vegetable and animal oils, and greases made from them, are nitrated by mixed acid with more or less rapid evolution of gases. *It is positively dangerous to use any such lubricants for use with mixed acids.* Mineral oils and greases should be used.

10. **Protection of Coils at Air Acid Level.**—When steel cooling coils protrude through the lid of the mixing tank there is excessive corrosion of inlet and exit pipes owing to the action of nitric acid fumes. If sleeves of mild steel are welded round the pipes at these places, the life of a coil is considerably lengthened. A sleeve welded over a hole on a coil serves to make it once more effective.

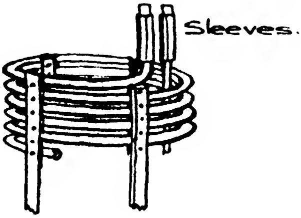

FIG. 117.—Top Portion of a Cooling Coil showing Welded-on Sleeves.

11. **Inlet Pipes.**—It is important to arrange inlet pipes to mixing tanks so that entering acids do not fall direct on to cooling coils. They should be continued to within a short distance of the bottom of the mixing tank to prevent splashing.

12. **Buildings.**—Buildings used for housing mixing plant should be built of wood well treated with creosote. A ruberoid type of roofing material is suitable for covering the roof boards (see Chapter II., p. 93). Galvanised iron should be avoided.

13. **Drains.**—As far as possible drains should be open channels, so that they can be easily accessible.

14. **Floors.**—Flooring is best carried out in acid-proof bricks or slabs, truly laid on concrete by the use of Trinidad asphalt, the joints being well rubbed with hot irons.

Conditions for Efficiency.

A mixing plant can work to nearly 100 per cent. efficiency if sufficient attention be paid to small details.

Drips.—A loss frequently overlooked because of its apparent smallness is due to drips.

1 drop of mixed acid per second = (say) 0.03 cub. in. per second.
= 0.42 oz. ,,
= 1 ton per day.

Any drip, however slight, should receive immediate attention. Apart from the loss of acid, drips inevitably cause serious destruction of plant and structure. Drips may be looked for at the following points:—

Pipe Lines.—(*a*) In steel lines at flanges and screwed joints. A leak is generally preceded by signs of sulphating. When there is any sign of corrosion the line should be drained and repaired.

(*b*) Lead lines often become thin and weak and should be watched.

(*c*) Earthenware lines need watching at all joints. A leak is generally preceded by "sweating." The line should be drained and the joint remade.

Earthenware Cocks.—Many earthenware cocks drip slightly, due to the plug not being ground perfectly to fit the cock. In such cases plugs should be ground in until drip-proof. It is well worth the expense to fit earthenware trays under the cocks to catch drips, though of course it is better to prevent them. These trays should lead by a 1-in. earthenware line to a carboy. Earthenware carboys are much safer to handle and are more durable than those made of glass. The cocks need attention. The plugs should be taken out, cleaned, and greased at least once weekly.

Metal Cocks.—A leak at the gland is an indication that it needs repacking. A crack in the case (or generally in any casting) is shown by sweating, which usually occurs before a drip shows itself. This should be looked for, and the faulty piece replaced.

Disposal.—All acid released by breaking of lines or opening up of pumps should be caught in suitable vessels and saved.

Mixed acid drips may be tipped into iron vessels (blow casks situated low are very convenient), but nitric acid drips must be tipped into an earthenware receiver or mixer. The tipping of carboys needs nothing but care to avoid accidents.

Leakage.—It is essential to test all valves regularly and systematically, otherwise acid may leak into or out of a mixer or other vessel. The outlet valves of the mixers may be tested by running the pump with all the outlet valves of the mixers closed off. If there is no diminution in level in the mixers the valves are tight. The inlet valves to the blenders may be tested by noting whether or not there is increase in dip in the blenders to which acid is not being pumped.

Fume.—A further possible source of loss in mixing is through fume. The following example will show what may be lost in this manner.

In a nitro-cotton mixing plant the four blenders, four R.V.A. tanks, and four spent tanks were connected with a fume line.

A portion of the fume was aspirated through a known solution of caustic soda, each test being run for twenty-four hours to ensure an average sample being obtained, and the alkalinity of the solution was then tested by titration. The speed of the fume was measured by Pitot tubes.

The following figures were obtained :—

Test.	Gas Aspirated.	HNO_3 Content.	HNO_3 Content per cubic foot.
1	1·7 cub. ft.	0·75 gram	0·44 gram
2	2·5 "	1·60 "	0.64 "
3	1·25 "	0·59 "	0·47 "

Average HNO_3 content = 0·54 gram per cubic foot.

The variation in HNO_3 content is due to :—

(*a*) Variation in plant working.

(*b*) Variation in atmospheric temperature—tests (1) and (3) were done in frosty weather, when there would be considerable condensation of fume in the pipes, acid so condensed running back to the tanks by gravity.

Three samples of condensed fume were obtained by aspirating fume through a U-tube surrounded by ice. The following analyses were obtained :—

Test.	1.	2.	3.
Per cent. HNO_3 . .	78·5	78·96	76·6
„ H_2SO_4 . .	1·2	1·1	1·2

The acid so produced is thus practically all nitric acid and is very corrosive.

The average velocity of gases through the pipe (6 in. internal diameter) was 23 ft. per second.

∴ Tonnage of acid passing per day = 0.203 ton
= 1.2 ton per week (6 days).

An absorption tower was erected (see p. 99) and the acid saved was found to vary between 0·9 and 1·4 ton of HNO_3 per week. The total cost of the tower was saved in the first week of running.

During the recent war years there was a decided change of attitude in chemical works in regard to acid fume. Prior to 1914 the question of elimination of fume to atmosphere was considered from an external standpoint. Very often the consideration was as to how much fume could be liberated to atmosphere without incurring penalties under the Alkali, etc., Works Regulation Act, without taking account of the actual loss of acid material, the destructive effect of the fume on plant and buildings, and the injurious effect on the health of workers. Faced primarily by the stern necessity of economising raw materials during the war, acid manufacturers came to be very zealous in controlling the emission of acid fume.

In acid-mixing practice, where it is possible to connect fume lines to vessels holding nitric acid, either free or mixed with sulphuric acid, this should be done.

Sludge in Mixed Acid—Samples of mixed acid show a milky appearance due to sludge and suspended matter, mainly ferric sulphate. Tests have shown that the heavier portion settles to the bottom in twenty-four hours, but after that the rate of settling is very slow. A 1-in. glass tube, 9 ft. high, was filled with mixed acid and allowed to stand. At the end of a month only the top 3 in. were perfectly clear, the remainder being quite milky in appearance. The exact influence of lighter suspended matter on nitrations has not been investigated, as no ill effects have been noted.

When a tank is put out of commission all sludge that will run out is saved in drums and used in the nitric acid retorts, where the HNO_3 distils off and the H_2SO_4 present is used in the reaction with the nitrate of soda. The average total acidity of several samples of sludge was approximately 60 per cent. (expressed as H_2SO_4).

It will be found that a considerable portion of the sludge in tanks can only be removed by the full force of water from a fire-hose. This represents inevitable loss due to formation of ferric sulphate by continuous reaction between the mixed acids and steel vessels.

Calibration of Vessels.

If all vessels which are used in the handling of raw and finished acids are correctly calibrated, the acid-mixing process is rendered much simpler and more certain. The time which has to be devoted to calibration purposes has only to be spent once, and the comfort and security resulting from knowing tonnages accurately are of great benefit.

Naturally, if it is possible to weigh the acids direct, the whole question of tank calibration is avoided.

The volumes of tanks are usually found by mathematical calculation or by running known weights of water into or from the tanks. The mathematical method is not always applicable, and the second method is slow and laborious.

Another method which can be used is to fill a tank with water, stir in a known weight of a soluble salt and then analyse a sample of the solution.

A method recently developed depends on the principle that water, flowing through a tube or orifice under a constant head, gives a constant rate of flow. J. W. M'David[1] describes the use of a handy calibrating apparatus devised on this principle.

To instance in some measure the degree of accuracy which can be worked to in handling large quantities of acids through

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1922, **41**, 295-96.

many differently shaped and sized vessels, the experience of working on the Acids Section at H.M. Factory, Gretna, where careful attention was paid to calibration, may be quoted.

In one case hundreds of tons of oleum were exported. This acid was stored in large 30 ft. by 9 ft. cylindrical boiler tanks. For plant stock purposes the total tonnage in the storage system was carefully kept. The oleum was transported from the factory in railway tank wagons which were weighed on two weigh-bridges, on one empty and on the other filled. Over a considerable period it was found that the tonnage of exported acid as registered by reduction of plant stocks was always more than that registered over the weigh-bridge. The latter tonnage was the one credited to the plant, and this necessitated reduction of registered stocks with consequent reaction on plant efficiency. After all other possible sources of discrepancy had been considered, the outgoing weigh-bridge was found to be inaccurate, registering approximately 1 per cent. short weight.

The second case concerned the acid-mixing department. Great trouble was experienced over a considerable period of time in balancing stocks of acid handled by the mixing department. Balance sheets invariably indicated a gain of H_2SO_4, and an approximately corresponding loss of HNO_3 after mixing the raw acids. Close investigation on the plant showed slight errors in calibration, and indicated the need for determining the gravity of acids at the time of dipping when calculating tonnages from dip measurements. The righting of these points resulted in a reduction of the discrepancies from about 1·5 per cent. to rather less than half that figure, reckoned on the H_2SO_4 tonnage. Further investigation on the plant proved fruitless, but the method of analysis was investigated. By making experimental mixes in the laboratory, using all precautions, it was found that the then accepted analytical method, using the nitrometer for determination of total nitrogen acids, did not give a balance of H_2SO_4 and HNO_3 between the raw and mixed acids. From results of careful experimentation with known acids in the laboratory, it was decided to adjust the analytical method for mixed acids to the extent of adding a 1 per cent. correction to all nitrometer readings. With the introduction of this correction, the mixing plant could render proper account of the raw materials used in the mixed acids produced.

Theoretical Calibration of a Cylindrical Storage Tank lying Horizontally.

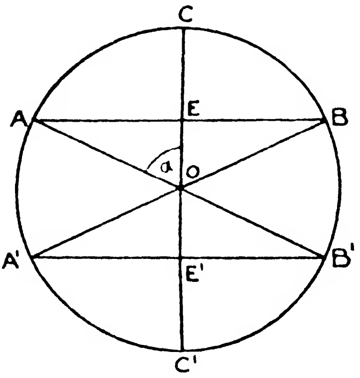

FIG. 118.

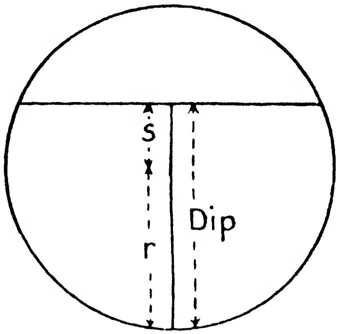

FIG. 119.

$$\text{Let } OE = s = EC' - \text{radius}$$
$$OE' = -s = E'C' - \text{,,}$$
$$\textit{i.e.}\quad s = \text{Dip} - \text{radius}.$$

The volumes of liquid at depths $E'C'$ and EC are dependent on the areas $A'E'B'C'A'$ and $AEBB'C'A'A$ respectively.

$$\text{Area } AEBB'C'A' = \text{Area of circle} - \text{Area of sector } ACBOA + \text{Area of triangle } ADO$$
$$= \pi r^2 - \left(\pi r^2 \times \frac{a}{\pi}\right) + sr \sin a$$
$$= \pi r^2 - ar^2 + sr \sin a$$
$$\cos a = \frac{s}{r} \quad \therefore a = \cos^{-1}\frac{s}{r}$$
$$\therefore \frac{\text{Area}}{r^2} = \pi - \cos^{-1}\frac{s}{r} + \frac{s}{r}\sin\cos^{-1}\frac{s}{r}$$
$$= \phi \text{ say.}$$
$$\therefore \frac{\text{Volume}}{lr^2} = \phi$$
$$\text{and Volume} = l\phi r^2.$$

ϕ may now be carefully plotted on a large scale graph for values of $\frac{s}{r}$ and the resulting graph can be used for making a table of volumes for the tank, at depths of successive eighths or tenths of an inch.

References—For calibration of cylindrical tanks lying horizontally, see S. W. Maher, *J. Ind. Eng. Chem.*, 1916, **8**, 636-7.

For calibration of cylindrical tanks not lying quite horizontal, see H. W. Wrigley, *J. Ind. Eng. Chem.*, 1916, **8**, 522-3.

For calibration of horizontal cylindrical tanks with spherical ends, see L. E. Carpenter, *J. Ind. Eng. Chem.*, 1914, **6**, 517, and K. B. Howell, *J. Ind. Eng. Chem.*, 1916, **8**, 430-3.

PROPERTIES OF MIXED ACIDS.

Specific Gravities.

The general trend of the specific gravity when nitric acid is mixed with sulphuric acid is shown in the following table, due to Marshall (Explosives):—

Specific Gravities of Mixed Acids (Marshall).

HNO_3.	Sp. Gr. 18°/18° in Air.	HNO_3	Sp. Gr. 18°/18° in Air.
Per cent.		Per cent	
0·00	1·8437	22·51	1·8215
0·52	1·8456	25·56	1·8112
1·05	1·8476	27·29	1·8053
4·67	1·8586	32·53	1·7863
7·17	1·8618	37·03	1·7700
7·37	1·8620	39·49	1·7601
7·75	1·8619	57·78	1·6879
9·10	1·8605	72·89	1·6227
11·33	1·8557	90·76	1·5408
12·71	1·8520	98·19	1·5080
16·52	1·8414	100·00	1·5009

Boiling-Points.

Boiling-points of mixed acids are given in Chapter VI., p. 333.

ANALYSIS.

The nitrometer method for the determination of total nitrogen acids, as herein described, is a rapid and accurate method for the analysis of a mixed acid, but it should be borne in mind that both speed and accuracy depend on attention to detail.

Preparation of Samples.

The sample as received is thoroughly mixed by shaking, and a portion transferred to a small glass-stoppered specimen jar for purposes of analysis.

Specific Gravity.

A further portion of the thoroughly mixed sample is poured into a hydrometer cylinder and the specific gravity observed by means of a carefully calibrated hydrometer. The hydrometer correction is applied and the specific gravity finally corrected to 15·5° C.

Total Acidity.

The total acidity is estimated by titration with normal sodium hydroxide solution and expressed as sulphuric acid (H_2SO_4).

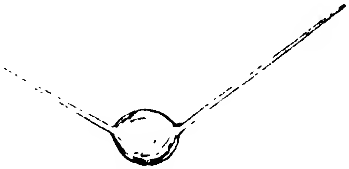

FIG. 120.—Oleum Bulb.

A quantity of acid sufficient to require from 30 to 40 c.c. of normal soda for its neutralisation is weighed in a small glass bulb (made from narrow bore glass tubing), which is then dropped into a clear glass wide mouth bottle of 16 oz. capacity containing 150 c.c. of distilled water, and broken by means of a glass rod, care being taken to break up the capillaries of the bulb so that all the acid goes rapidly into solution.

Normal sodium hydroxide is run in from a burette at a rate not greater than 30 c.c. per minute, but as the indicator used (methyl orange) is readily destroyed by nitrous acid, this is not added until titration is almost complete. During titration the burette jet is rested on the inside of the bottle and the alkali allowed to run down the sides; after the addition of the indicator the sides of the bottle are washed down with a fine jet of water from a wash bottle and the titration completed as rapidly as possible, adding the soda a drop at a time.

It is important that only sufficient indicator be added to give a decided colour, as an excess destroys the delicacy of the end point. It is good practice to add two drops of a solution containing 0·05 gram of methyl orange per 100 c.c. The end point is readily detected by comparing the tint of the solution with that of a standard made by passing CO_2 into 200 c.c. of distilled water containing two drops of 0·05 per cent. methyl orange solution. The end point being reached, the burette is allowed to drain for two minutes and an observation of the reading taken.

A burette correction obtained by reference to the calibration certificate for the burette in use is applied to the reading, and also a temperature correction to allow for the error, due to variation of the normal soda in the burette from standard value.

If standard solutions are prepared at 20° C. and the burettes are calibrated to deliver Mohr cubic centimetres at the same temperature, for each 50 c.c. titration 0·015 c.c. are subtracted from the burette reading for each degree Centigrade above 20° C., or in general work for normal titrations of from 30 to 40 c.c., 0·05 c.c. are subtracted from the reading for every 5° C. below the standardisation temperature (20° C.).

Total Nitrogen Acids.

The total nitrogen acids are estimated by means of the nitrometer. A quantity of acid, varying with the nature of the mixed acid being analysed, is weighed by difference into the cup of the calibrated nitrometer to which 2 c.c. of H_2SO_4 has previously been added. A Lunge-Rey pipette is used for this purpose, and it is given a preliminary washing out with the acid before proceeding with the weighing.

The sample is then run into the nitrometer and the cup thoroughly washed by five successive washings of 2 c.c. of sulphuric acid, each followed by a sixth washing of 5 c.c. The acid used for this purpose is pure concentrated nitrogen-free sulphuric acid which has been diluted to a strength of 94·5 per cent. acid. In washing out the cup special care is taken to prevent any loss of nitric oxide and to completely wash down the sides of the cup and drain the entire washings into the nitrometer.

The decomposition is effected by shaking the nitrometer while held in an almost horizontal position, care being taken that the evolved gas is kept under slight suction and that no gas or acid reaches the rubber tubing of the nitrometer. The tube is shaken for one or two minutes until no more gas is evolved. The two tubes are then placed so that the mercury in the decomposition tube is as much higher than that in the pressure tube as is necessary to compensate for the layer of acid in the latter; 1 mm. of mercury is allowed for every 7 mm. of acid.

After allowing to stand for five minutes, a final shake of half a minute is given.

The tube is now set up and adjusted so that the gas is under very slight suction, and allowed to stand for thirty minutes in order that the temperature may become equalised. The pressure is then exactly adjusted by pouring (if necessary) a drop of acid into the cup and cautiously opening the tap. By noting whether the gas is under pressure or suction, and by altering the level of the pressure tube accordingly, the pressure of the gas can be exactly equalised with atmospheric pressure, so that when the nitrometer tap is opened the drop of acid in the bore of the tap remains quite stationary. After decomposition of the nitric acid has been effected, care should be taken to keep the hands and body as clear as possible from the gas in the decomposition tube to prevent errors due to expansion.

The volume of the gas, the barometric pressure, and the temperature are then observed; the latter by means of a standardised thermometer suspended in close proximity to the decomposition bulb of the nitrometer. The barometric reading should be corrected for the index error of the instrument, temperature of mercury and scale, latitude, altitude, capillarity and vapour pressure of mercury, and it is well to have these corrections embodied in a table for commonly met barometric readings.

Correction for temperature of mercury and scale at 20° C. is - 2.5 mm.
Correction for latitude at Edinburgh (56° N.) is + 0.7 mm.

It will be observed that the contents of the decomposition tube after the completion of a determination occasionally form a tenacious emulsion which adheres to the sides of the bulb and tube, and reading of the gas volume becomes difficult.

Care in the use of sulphuric acid for decomposition is necessary to avoid this difficulty. If less than the recommended quantity be used, the bulb and tube become coated with mercurous sulphate, and an emulsion of mercury, mercury salt, and acid is also formed.

The difficulty may be partly overcome by washing down the bulb and tube with fresh acid after decomposition has been effected. However, this practice is to be avoided because the acid added will absorb an uncertain amount of nitric oxide.

Care and practice tend to overcome such difficulties.

The observed volume of the gas is reduced to N.T.P. and the result calculated as percentage of nitric acid (HNO_3). One c.c. of NO gas at N.T.P. corresponds to 2·8144 mg. HNO_3, so that the total nitrogen acids expressed as nitric acid is given by the formula

$$\frac{v \times 0.0028144 \times 100}{w}$$

where v represents the observed volume of the gas and w the weight of mixed acid taken.

A "solubility" correction is applied to allow for the solubility of nitric oxide gas in sulphuric acid. This correction, which is an empirical one, amounts to 1 per cent. of the percentage of total nitrogen acids expressed as nitric acid.

If, for example, after all the other corrections have been applied, the nitrometer indicates the presence in a mixed acid of 23·00 per cent. of total nitrogen acids, the solubility correction will amount to 1 per cent. of this value, that is, 0·23, and the figure returned will be 23·2 per cent. of total nitrogen acids.

The "Solubility Correction."—Statistics of acid movement through the Mixing Department at H.M. Factory, Gretna, having shown that in the preparation of mixed acid on the large scale there was an apparent loss of nitric acid and a gain of sulphuric acid, investigation was set afoot to see if such a state of affairs could be attributed to the methods of analysis. Mr J. S. Hill of the Chemical Department carried out the investigation, which is recorded in Experimental Report, No. 114, Dornock, H.M. Factory, Gretna.

Carefully analysed nitric and sulphuric acids were mixed in the laboratory with all due care. The mixed acids so prepared were analysed by the nitrometer with results which did not agree with the computed results. In each case the total nitrogen acids content of the mixture was in the region of 1 per cent. lower than the content charged.

Nitrous Acid.

The nitrous acid content is determined by titration against potassium permanganate solution. Ten c.c. of semi-normal potassium permanganate are pipetted into a 500 c.c. Erlenmeyer flask containing 200 c.c. of distilled water. The solution is heated to 20-40° C., and the acid to be analysed is then run in slowly from a burette until the colour almost vanishes. The end point aimed at is a faint pink tint which should remain unchanged for about two minutes.

The amount of nitrous acid present is then calculated from the number of cubic centimetres of acid used in the titration.

Nitric Acid.

The percentage of nitric acid is obtained by subtracting the nitrous acid (expressed as HNO_3) from the total nitrogen acids (also expressed as HNO_3). To this end the percentage of nitrous acid is multiplied by 1·34, which represents the ratio between equivalent weights of nitric and nitrous acid,

$$\frac{HNO_3}{HNO_2} \quad \frac{63.018}{47.018} = 1{\cdot}34$$

and the value obtained subtracted from the percentage of total nitrogen acids calculated as nitric acid in the manner already indicated.

Sulphuric Acid.

The percentage of sulphuric acid present in the sample is obtained by subtracting the value for the total nitrogen acids expressed as sulphuric acid from the total acidity expressed in similar terms. For this purpose the percentage of total nitrogen acids expressed as nitric acid (HNO_3) is multiplied by the fraction $\frac{7}{9}$ which represents the ratio between equivalent amounts of sulphuric and nitric acids,

$$\frac{\frac{1}{2}\,H_2SO_4}{HNO_3} = \frac{49.038}{63.018} = \frac{7}{9}$$

and the value obtained subtracted from the total acidity calculated as sulphuric acid in the manner already indicated.

Water.

The percentage of water present in the sample is obtained by difference, *i.e.*, by subtracting the sum of the sulphuric acid, nitric acid, and nitrous acid percentages from 100.

REFERENCES.

Specific Gravities.

Pascal and Garnier.—*Bull. Soc. chim.*, 1919 ; [IV], **25**, 142-5 ; *J. Chem. Soc. Abstr.*, 1919 ; [II], **116**, 229.
Elwyn Roberts.—*J. Soc. Chem. Ind.* (*Trans.*), 1921, **40**, 165-6.
Marshall.—"Explosives."

Properties.

Saposchnikoff.—*J. Russ. Phys. Chem. Soc*, 1903, **35**, 1098-1112 ; *J. Chem. Soc. Abstr.*, 1904 ; [II], **86**, 251 ; *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 518-32 ; *J. Chem. Soc. Abstr.*, 1904 ; [II], **86**, 558 ; *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 669-71 ; *J. Chem. Soc. Abstr.*, 1904 ; [II], **86**, 614.
Schaeffer and Niggemann.—*Z. anorg. Chem.*, 1916, **98**, 77-85 ; *J. Chem. Soc. Abstr.*, 1917 ; [II], **112**, 186.
Kaltenbach.—*Chimie et Industrie*, 1918, **1**, 81-4.

Distillation.

Pascal.—*Comptes rend.*, 1917, **165**, 589-91 ; *J. Soc. Chem. Ind.*, 1917, **36**, 1232.
Baumann.—*Chem. Zeit.*, 1920, **44**, 805.
Pascal.—*Chem. and Met. Eng.*, 1921, **25**, 1103-6.
Pascal and Garnier.—*Bull. Soc. chim.*, 1919, **25**, 142 ; 1920, **27**, 8.
Galle.—*Z. angew. Chem.*, 1921, **34**, 168-70 ; 173-5 ; *Chem. and Met. Eng.*, 1921, **25**, 741-6.
Berl and Samtleben.—*Z. angew. Chem.*, 1922, **35**, 201-2 ; 206-11.

Boiling-Points.

Pascal.—*Bull. Soc. chim.*, 1920 ; [IV], **27**, 814-20 ; *J. Chem. Soc. Abstr.*, 1920 ; [II], **117**, 752.

Analysis.

Pitman.—*J. Soc. Chem. Ind.*, 1900, **19**, 982-4.
W. H. **Patterson.**—*J. Soc. Chem. Ind.* (*Review*), 1922, **41**, 496-8.

Action on Iron.

Cumming.—*J. Soc. Chem. Ind.* (*Trans.*), 1919, **88**, 31-2.

Freezing-Point.

Holmes.—*J. Ind. Eng. Chem.*, 1920, **12**, 781-3.

Specific Heats.

Pascal and Garnier.—*Bull. Soc. chim.*, 1920; [IV], **27**, 8-18; *J. Chem. Soc. Abstr.*, 1920; [II], **118**, 162.

Absorption Spectra.

Schaeffer and Niggemann.—*Z. anorg. Chem.*, 1916, **98**, 77-85; *J. Chem. Soc. Abstr.*, 1917; [II], **112**, 186.

Calculations.

Clément.—*Le Caoutchouc et La Gutta-Percha*, 1907, **3**, 3019.
Fowler.—*J. Soc. Chem. Ind.* (*Trans.*), 1919, **88**, 34-6; *ibid.*, 1921, **40**, 166-7.
Young.—*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 315-16.

Acid Mixing.

Acid Mixing.—"Technical Records of Explosives Supply, 1915-18. No. 1. H.M. Stationery Office."

Calibration.

S. W. **Maher.**—*J. Ind. Eng. Chem.*, 1916, **8**, 636-7.
H. W. **Wrigley.**—*J. Ind. Eng. Chem.*, 1916, **8**, 522-3.
L. E. **Carpenter.**—*J. Ind. Eng. Chem.*, 1914, **6**, 517.
K. B. **Howell.**—*J. Ind. Eng. Chem.*, 1916, **8**, 430-3.
J. W. **M'David.**—*J. Soc. Chem. Ind.* (*Trans.*), 1922, **41**, 295.

Heat Developed.

J. W. **M'David.**—*J. Soc. Chem. Ind.* (*Trans.*), 1922, **41**, 246.

CHAPTER VI

PHYSICAL AND CHEMICAL PROPERTIES OF NITRIC ACID

HISTORICAL.

NITRIC acid has been known from very early times. In 778 A.D. Geber described its preparation by strongly heating a mixture of saltpetre, alum, and sulphate of copper. Glauber, in the seventeenth century, prepared it by distilling nitre with oil of vitriol.

Nitric acid was commonly used by alchemists, especially as a means of separating gold and silver. It went under various names, such as aqua fortis, spiritus nitri acidus, and spiritus nitri fumans Glauberi.

Lavoisier (1776) showed that nitric acid contained oxygen,[1] whilst a few years later Cavendish showed it to contain nitrogen on preparing it by passing electric sparks through mixtures of nitrogen and oxygen.[2]

OCCURRENCE.

Nitric acid occurs naturally, in traces only, in the atmosphere and in rain-water.[3] The presence of nitric acid in the air is no doubt due to atmospheric electrical discharges. Rain-water carrying traces of nitric acid leads to the formation of salts on passing on to the ground. Nitrates (as these salts are called) are thus found widely distributed but usually only in minute quantities.

Nitric acid results from the natural oxidation of animal nitrogenous organic matters, and the acid in presence of water

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[1] Lavoisier, *Œuvres*, ii., 226.

[2] *Phil. Trans.*, 1784, p. 119, and 1785, p. 372.

[3] Warrington, *J. Chem. Soc. Trans.*, 1889, **55**, 537.

combines with earth bases to form nitrates. The presence of nitrates in natural waters is largely due to this series of reactions.

Nature provides a few instances of large scale nitric acid and subsequent nitrates production, the most noted being the deposits of nitrate of soda in Chili and those of nitrate of potash in India.

FORMATION.

1. By burning hydrogen in the air, or in oxygen in the presence of nitrogen.

2. By burning air in coal-gas and coal-gas in air.

L. T. Wright points out that nitric acid formation in the latter instance may not be due to oxidation of nitrogen but to oxidation of ammonia present as an impurity in the air.[1]

3. By passing electric sparks for some time through a mixture of moist nitrogen and oxygen.

4. Nitrogen and oxygen combine in the presence of water or dilute alkalis, at the ordinary temperature, under the influence of a silent electric discharge, to give nitric acid.

$$2N_2 + 5O_2 + 2H_2O + Aq = 4HNO_3 \text{ dil.}$$

5. By oxidation of ammonia.

6. By the interaction of nitrogen peroxide with sulphuric acid.[2]

7. By oxidation of ammonia, resulting from the decomposition of animal nitrogenous organic matter, through the medium of nitrifying bacteria.

8. During the slow oxidation of ether and phosphorus in the air in presence of water.[3]

PREPARATION.

1. A mixture of dry potassium nitrate with an equal weight of concentrated sulphuric acid is distilled from a glass retort at as low a temperature as possible. The volatile nitric acid

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[1] *J. Chem. Soc. Trans.*, 1879, **35**, 42-46.

[2] Lunge, *Ber.*, **12**, 1058.

[3] Berthelot, *Comptes rend.*, **108**, 543.

which distils over is condensed in a well-cooled receiver, and potassium hydrogen sulphate is left in the retort.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

The distillate has a yellow colour due to the presence of nitrogen peroxide in solution. It also contains water which may be due to the fact that nitric acid decomposes partially on heating,

$$4HNO_3 = 4NO_2 + 2H_2O + O_2$$

or to this fact and to the presence of water in the reacting materials in the retort.

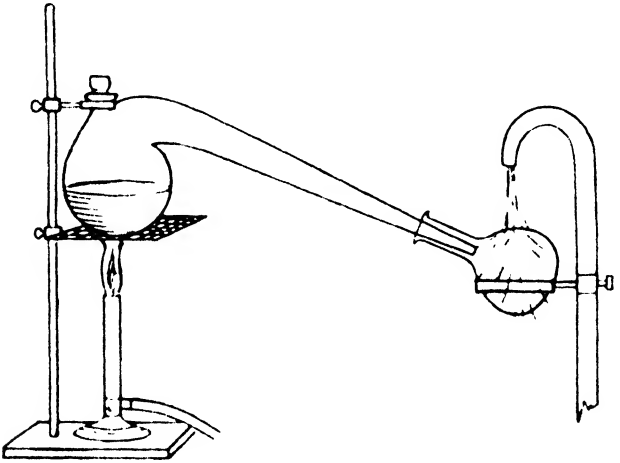

FIG. 121.—Laboratory Preparation of Nitric Acid.

Pure Acid.

To purify the acid thus obtained it is redistilled with the addition of its own volume of concentrated sulphuric acid at a low temperature. This second distillate is then freed from dissolved nitrogen peroxide by gently warming and then passing a current of dry air through it until it is cold. By such a method of preparation, Roscoe obtained acid of 99·5 to 99·8 per cent. HNO_3 content.[1]

Veley and Manley obtained a still purer acid by distilling ordinary concentrated acid under diminished pressure with

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[1] *J. Chem. Soc. Trans.*, 1861, **13**, 146.

small amounts of barium and silver nitrates to remove traces of sulphuric and hydrochloric acids. The distillate was then treated with a stream of ozonised oxygen to remove nitrous acid and again distilled under diminished pressure. Finally, the distillate was redistilled in a sealed and evacuated apparatus.[1]

Absolute nitric acid exists only in the form of snow-white crystals below −41° C. On melting, it decomposes partially into N_2O_5 and water which dissolve in the acid to a yellow solution. On passing a current of dry air through the solution the N_2O_5 is removed, until a colourless acid containing 98·67 per cent. HNO_3 is left, which volatilises unaltered.[2]

Physical Properties of Nitric Acid.

Appearance.

Absolute nitric acid, HNO_3, is described above.

Aston and Ramsay describe nitric acid of 99·8 per cent. HNO_3 as having a very pale yellow colour and fuming strongly on exposure to the air.[3]

Commercial pure nitric acids contain varying proportions of water and vary in colour from very pale straw colour to orange, owing to the presence of lower oxides of nitrogen in solution.

Smell.

Nitric acid has a peculiar, pungent, but not very powerful smell.

Specific Gravity.

The work of Veley and Manley[4] on the specific gravities of nitric acid and its aqueous solutions in general confirmed the previous determinations of Lunge and Rey.[5]

The accompanying table is from the work of Lunge and Rey. The specific gravities are for chemically pure nitric acid; commercial acid containing nitrous acid, etc., contains less real HNO_3 at the same specific gravity.

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[1] *Phil. Trans.*, 1898, **191** A, 365.

[2] Küster and Münch, *Z. anorg. Chem.*, 1905, **48**, 350-55.

[3] *J. Chem. Soc. Trans.*, 1894, **65**, 169.

[4] *J. Soc. Chem. Ind.*, 1903, **22**, 1227.

[5] *Z. angew. Chem.*, 1891, p. 165.

Specific Gravities at $\frac{15°}{4°}$.	Degrees Twad.	100 parts by weight contain		1 litre contains kg.	
		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·000	0	0·08	0·10	0·001	0·001
1·005	1	0·85	1·00	0·008	0·010
1·010	2	1·62	1·90	0·016	0·019
1·015	3	2·39	2·80	0·024	0·028
1·020	4	3·17	3·70	0·033	0·038
1·025	5	3·94	4·60	0·040	0·047
1·030	6	4·71	5·50	0·049	0·057
1·035	7	5·47	6·38	0·057	0·066
1·040	8	6·22	7·26	0·064	0·075
1·045	9	6·97	8·13	0·073	0·085
1·050	10	7·71	8·99	0·081	0·094
1·055	11	8·43	9·84	0·089	0·104
1·060	12	9·15	10·68	0·097	0·113
1·065	13	9·87	11·51	0·105	0·123
1·070	14	10·57	12·33	0.113	0·132
1·075	15	11·27	13·15	0·121	0·141
1·080	16	11·96	13·95	0·129	0·151
1·085	17	12·64	14·74	0·137	0·160
1·090	18	13·31	15·53	0·145	0·169
1·095	19	13·99	16·32	0·153	0·179
1·100	20	14·67	17·11	0·161	0·188
1·105	21	15·34	17·89	0·170	0·198
1·110	22	16·00	18·67	0·177	0·207
1·115	23	16·67	19·45	0·186	0·217
1·120	24	17·34	20·23	0·195	0·227
1·125	25	18·00	21·00	0·202	0·236
1·130	26	18·66	21·77	0·211	0·246
1·135	27	19·32	22·54	0·219	0·256
1·140	28	19·98	23·31	0·228	0·266
1·145	29	20·64	24·08	0·237	0·276
1·150	30	21·29	24·84	0·245	0·286
1·155	31	21·94	25·60	0·254	0·296
1·160	32	22·60	26·36	0·262	0·306
1·165	33	23·25	27·12	0·271	0·316
1·170	34	23·90	27·88	0·279	0·326
1·175	35	24·54	28·63	0·288	0·336
1·180	36	25·18	29·38	0·297	0·347
1·185	37	25·83	30·13	0·306	0·357
1·190	38	26·47	30·88	0·315	0·367
1·195	39	27·10	31·62	0·324	0·378
1·200	40	27·74	32·36	0·333	0·388
1·205	41	28·36	33·09	0·342	0·399
1·210	42	28·99	33·82	0·351	0·409
1·215	43	29·61	34·55	0·360	0·420
1·220	44	30·24	35·28	0·369	0·430
1·225	45	30·88	36·03	0·378	0·441
1·230	46	31·53	36·78	0·387	0·452
1·235	47	32·17	37·53	0·397	0·463
1·240	48	32·82	38·29	0·407	0·475
1·245	49	33·47	39·05	0·417	0·486
1·250	50	34·13	39·82	0·427	0·498
1·255	51	34·78	40·58	0·437	0·509
1·260	52	35·44	41·34	0·447	0·521
1.265	53	36·09	42·10	0·457	0·533

Specific Gravities at $\frac{15^\circ}{4^\circ}$.	Degrees Twad.	100 parts by weight contain		1 litre contains kg.	
		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·270	54	36·75	42·87	0·467	0·544
1·275	55	37·41	43·64	0·477	0·566
1·280	56	38·07	44·41	0·487	0·568
1·285	57	38·73	45·18	0·498	0·581
1·290	58	39·39	45·95	0·508	0·593
1·295	59	40·05	46·72	0·519	0·605
1·300	60	40·71	47·49	0·529	0·617
1·305	61	41·37	48·26	0·540	0·630
1·310	62	42·06	49·07	0·551	0·643
1·315	63	42·76	49·89	0·562	0·656
1·320	64	43·47	50·71	0·573	0·669
1·325	65	44·17	51·53	0·585	0·683
1·330	66	44·89	52·37	0·597	0·697
1·335	67	45·62	53·22	0·609	0·710
1·340	68	46·35	54·07	0·621	0·725
1·345	69	47·08	54·93	0·633	0·739
1·350	70	47·82	55·79	0·645	0·753
1·355	71	48·57	56·66	0·658	0·768
1·360	72	49·35	57·57	0·671	0·783
1·365	73	50·13	58·48	0·684	0·798
1·370	74	50·91	59·39	0·698	0·814
1·375	75	51·69	60·30	0·711	0·829
1·380	76	52·52	61·27	0·725	0·846
1·385	77	53·35	62·24	0·739	0·862
1·390	78	54·20	63·23	0·753	0·879
1·395	79	55·07	64·25	0·768	0·896
1·400	80	55·97	65·30	0·783	0·914
1·405	81	56·92	66·40	0·800	0·933
1·410	82	57·86	67·50	0·816	0·952
1·415	83	58·83	68·63	0·832	0·971
1·420	84	59·83	69·80	0·849	0·991
1·425	85	60·84	70·98	0·867	1·011
1·430	86	61·86	72·17	0·885	1·032
1·435	87	62·91	73·39	0·903	1·053
1·440	88	64·01	74·68	0·921	1·075
1·445	89	65·13	75·98	0·941	1·098
1·450	90	66·24	77·28	0·961	1·121
1·455	91	67·38	78·60	0·981	1·144
1·460	92	68·56	79·98	1·001	1·168
1·465	93	69·79	81·42	1·023	1·193
1·470	94	71·06	82·90	1·045	1·219
1·475	95	72·39	84·45	1·068	1·246
1·480	96	73·76	86·05	1·092	1·274
1·485	97	75·18	87·70	1·116	1·302
1·490	98	76·80	89·60	1·144	1·335
1·495	99	78·52	91·60	1·174	1·369
1·500	100	80·65	94·09	1·210	1·411
1·501	...	81·09	94·60	1·217	1·420
1·502	...	81·50	95·08	1·224	1·428
1·503	...	81·91	95·55	1·231	1·436
1·504	...	82·29	96·00	1·238	1·444
1·505	101	82·63	96·39	1·244	1·451
1·506	...	82·94	96·76	1·249	1·457
1·507	...	83·26	97·13	1·255	1·464

Specific Gravities at $\frac{15^\circ}{4^\circ}$.	Degrees Twad.	100 parts by weight contain		1 litre contains kg.	
		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·508	...	83·58	97·50	1·260	1·470
1·509	...	83·87	97·84	1·265	1·476
1·510	102	84·09	98·10	1·270	1·481
1·511	...	84·28	98·32	1·274	1·486
1·512	...	84·46	98·53	1·277	1·490
1·513	...	84·63	98·73	1·280	1·494
1·514	...	84·78	98·90	1·283	1·497
1·515	103	84·92	99·07	1·287	1·501
1·516	...	85·04	99·21	1·289	1·504
1·517	...	85·15	99·34	1·292	1·507
1·518	...	85·26	99·46	1·294	1·510
1·519	...	85·35	99·57	1·296	1·512
1·520	104	85·44	99·67	1·299	1·515

Correction of the observed Specific Gravities for Temperatures a little above or below 15° C.

			Add for − 1° C. Deduct for + 1° C.
With sp. gr.	between	1·000 to 1·020	0·0001
,,	,,	1·021 ,, 1·040	0·0002
,,	,,	1·041 ,, 1·070	0·0003
,,	,,	1·071 ,, 1·100	0·0004
,,	,,	1·101 ,, 1·130	0·0005
,,	,,	1·131 ,, 1·160	0·0006
,,	,,	1·161 ,, 1·200	0·0007
,,	,,	1·201 ,, 1·245	0·0008
,,	,,	1·246 ,, 1·280	0·0009
,,	,,	1·281 ,, 1·310	0·0010
,,	,,	1·311 ,, 1·350	0·0011
,,	,,	1·351 ,, 1·365	0·0012
,,	,,	1·366 ,, 1·400	0·0013
,,	,,	1·401 ,, 1·435	0·0014
,,	,,	1·436 ,, 1·490	0·0015
,,	,,	1·491 ,, 1·500	0·0016
,,	,,	1·501 ,, 1·520	0·0017

The effect of dissolved nitrogen peroxide in raising the specific gravity of nitric acid is seen in the following table due to Lunge and Marchlewski,[1] which shows how the specific gravity of nitric acid (sp. gr. 1·4960 at $\frac{15^\circ}{4^\circ}$) is influenced by different percentages of N_2O_4.

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[1] *Z. angew. Chem.*, 1892, pp. 10, 330.

Influence of Nitrous Acid on the Specific Gravity of Nitric Acid (sp. gr. 1·4960 at $\frac{15^\circ}{4^\circ}$).

N_2O_4. per cent.	Alteration of sp. gr. of nitric acid by N_2O_4.	N_2O_4 per cent.	Alteration of sp. gr. of nitric acid by N_2O_4.
0·25	0·00050	6·55	0·04475
0·50	0·00075	7·00	0·04650
0·75	0·00150	7·25	0·04720
1·00	0·00300	7·50	0·05000
1·25	0·00475	7·75	0·05165
1·50	0·00675	8·00	0·05325
1·75	0·00775	8·25	0·05500
2·00	0·01050	8·50	0·05660
2·25	0·01250	8·75	0·05825
2·50	0·01425	9·00	0·06000
2·75	0·01625	9·25	0·06160
3·00	0·01800	9·50	0·06325
3·25	0·01985	9·75	0·06500
3·50	0·02165	10·00	0·06600
3·75	0·02350	10·25	0·06815
4·00	0·02525	10·50	0·06975
4·25	0·02690	10·75	0·07135
4·50	0·02875	11·00	0·07300
4·75	0·03050	11·25	0·07450
5·00	0·03225	11·50	0·07600
5·25	0·03365	11·75	0·07750
5·50	0·03600	12·00	0·07850
5·75	0·03775	12·25	0·08050
6·00	0·03950	12·50	0·08200
6·25	0·04175	12·75	0·08350
6·50	0·04300	...	...

The following graph (Fig. 122) giving specific gravities, Twaddell degrees, percentage HNO_3, grams HNO_3 per litre of solution, and lbs. HNO_3 per gallon of solution is based on figures by Lunge and Rey,[1] and is from *Physical and Chemical Data of Nitrogen Fixation*, published by the Ministry of Munitions, Munition Invention Department and Nitrogen Products Committee (December 1918).

Contraction on Mixing with Water.

When nitric acid and water are mixed, the maximum contraction takes place for the ratio $2HNO_3 : 3H_2O$.[2]

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[1] *Z. angew. Chem.*, 1891, p. 165.

[2] Kolb, *Ann. Chim. Phys.* [IV], **10**, 136.

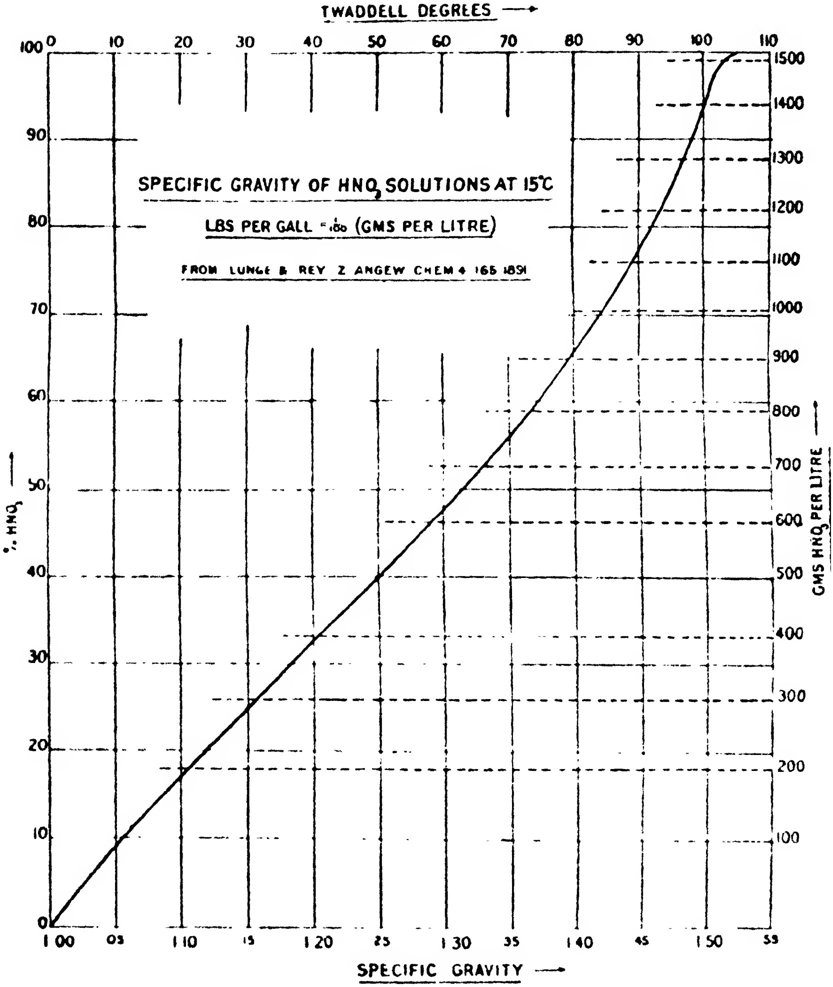
TWADDELL DEGREES →
0
10
20
30
40
50
60
70
80
90
100
110
SPECIFIC GRAVITY OF HNO_3 SOLUTIONS AT 15°C
LBS PER GALL = $\frac{1}{100}$ (GMS PER LITRE)
FROM LUNGE & REY Z ANGEW CHEM 4 165 1891
100
90
80
70
60
50
40
30
20
10
0
% HNO_3 →
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
GMS HNO_3 PER LITRE →
1 00
05
1 10
15
1 20
25
1 30
35
1 40
45
1 50
55
SPECIFIC GRAVITY →

FIG. 122.

The following table of contractions is a selection from the work of Veley and Manley.[1]

Percentage HNO_3.	Temperature °C.	Contraction.
19·37	14·2	·03685
20·68	"	·03849
21·98	"	·04087
25·50	"	·0465 *
30·17	24·2	·05171
32·82	"	·05510
33·87	"	·05571
42·40	14·2	·0669 *
52·80	"	·0704 *
60·60	"	·06592
62·84	"	·06399
65·80	"	·06104
70·20	"	·05680
78·22	"	·04528
81·97	"	·03709
87·90	"	·02500
89·73	"	·02154
92·34	"	·01626
94·04	"	·01130
95·62	"	·00672
99·97	"	·00008

* Taken from curves.

Boiling-Point.

The boiling-point of the purest liquid nitric acid at atmospheric pressure is given by Roscoe as 86° C., but decomposition occurs before this temperature is reached.[2]

The influence of pressure on the boiling-point is seen in the accompanying table, due to Creighton and Githens.[3]

99·79 per cent. HNO_3.

Pressure, mm. Hg.	Boiling-point, degrees.	Pressure, mm. Hg.	Boiling-point, degrees.
47	22·1	290	57·1
51	24·5	346	62·1
60	26·2	360	63·4
90	31·7	425	68·5
110	35·6	500	72·7
125	38·5	580	77·2
203	49·0	675	82·5
250	53·5	...	...

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[1] *Roy. Soc. Proc.*, **69**, 86-119; *J. Chem. Soc. Trans.*, 1903, **88**, 1015-1021.

[2] Roscoe, *J. Chem. Soc. Trans.*, 1861, **18**, 146.

[3] *J. Franklin Inst.*, 1915, **179**, 161.

The results are shown graphically in Fig. 123, which also gives graphs for the data concerning aqueous solutions of nitric acid.

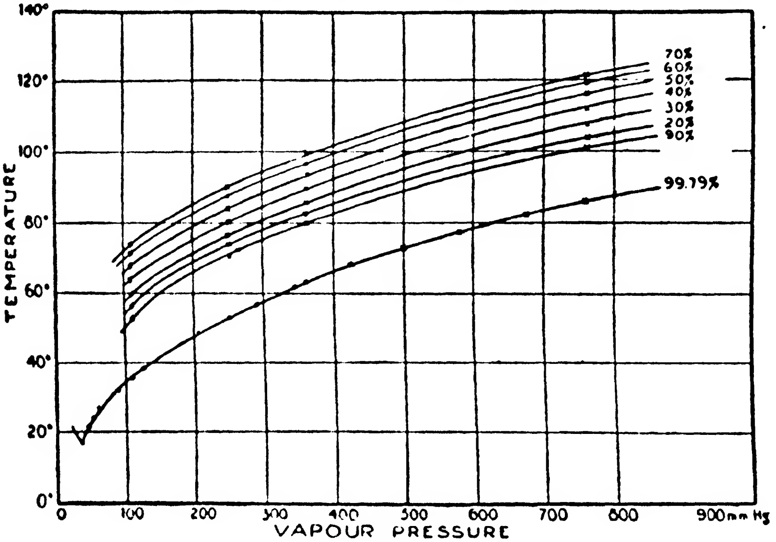

FIG. 123.—Boiling-points of HNO_3 (99·79 per cent.), and Aqueous Solutions at Different Pressures.

The boiling-points of aqueous solutions of nitric acid at 760 mm., 360 mm., 250 mm., and 110 mm. pressure, and their composition, are given in the following table (Creighton and Githens):—

Pressure 760 mm.		Pressure 360 mm.		Pressure 250 mm.		Pressure 110 mm.	
Per cent. HNO_3.	Boiling-point, degrees.	Per cent. HNO_3	Boiling-point, degrees.	Per cent. HNO_3	Boiling-point, degrees	Per cent. HNO_3	Boiling-point, degrees.
19·37	103·56	20·30	84·7	19·51	74·5	23·61	57·5
30·43	108·08	32·05	87·2	30·02	76·6	34·54	60·7
41·38	112·59	42·75	91·1	45·42	82·1	40·44	63·6
51·63	116·85	53·14	95·4	56·91	86·4	51·74	68·3
56·01	118·88	54·67	95·8	65·34	89·4	54·42	69·4
59·77	120·06	57·72	97·2	67·91	89·9	60·21	71·6
63·89	121·27	61·26	98·7	68·72	89·9	66·78	74·3
65·17	121·66	67·25	100·0	71·24	89·6	68·32	73·9
67·74	121·67	68·46	99·8	79·50	83·1	68·53	73·6
68·18	121·79	68·91	99·9	87·93	70·4	69·42	73·8
69·24	121·80	69·61	99·9	90·04	69·5	73·12	73·1
71·10	121·60	74·39	99·6	95·76	59·1	80·61	66·8
73·56	120·75	76·92	97·4	99·79	53·5	87·62	56·5
80·50	115·45	80·21	94·0	...	...	94·31	45·0
85·51	108·12	84·41	89·1	...	...	99·79	35·6
90·06	102·03	91·31	79·5	...	...	...	...
95·45	95·42	99·79	63·4	...	...	...	...

The change of boiling-point with variation of concentration at constant pressures is shown in Fig. 124.

Solution of Constant Boiling-point.—Dalton was the first to point out that whether concentrated or dilute aqueous solutions of nitric acid are distilled at atmospheric pressure, the boiling-point gradually rises to 120·5° C., when the liquid thus obtained distils over unchanged at this constant temperature. The solution of constant boiling-point contains 68 per cent. HNO_3 and has a specific gravity of 1·414 at 15·5° C. Roscoe examined this solution and found that if it is distilled under increased or diminished pressure its composition changes, and for each pressure the solution of constant boiling-point has a different concentration.

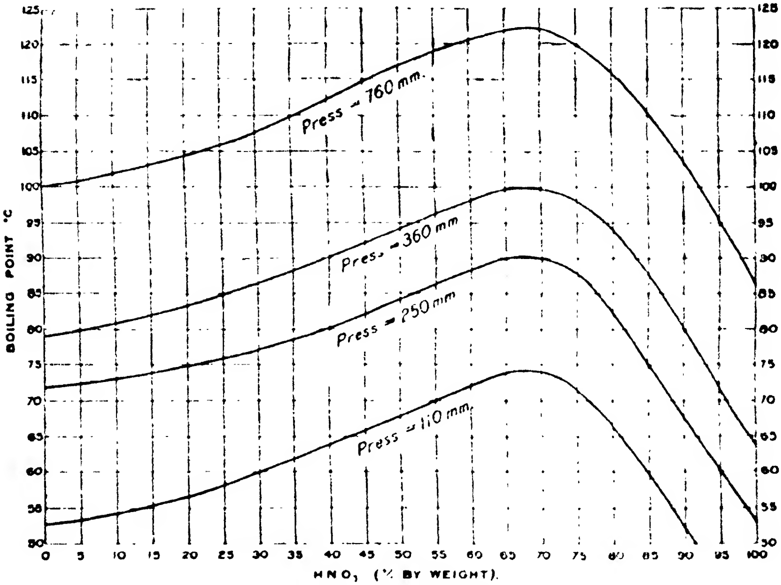

FIG. 124.—Boiling-points of Aqueous Nitric Acid under Constant Pressures.

This points to the fact that the solution of 68 per cent. HNO_3 content is not a definite hydrate of nitric acid. If it were, it should preserve its constant composition throughout a definite range of temperature and pressure.[1]

Effect of Sulphuric Acid on.—The effect of sulphuric acid

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[1] Roscoe, *J. Chem. Soc. Trans.*, 1861, 18, 146.

on the boiling-point of nitric acid is shown in Fig. 125, due to Creighton and Smith.[1] It is seen that the presence of sulphuric acid raises the boiling-point of nitric acid solutions and leads to a decrease in the HNO_3 content of the mixture of constant boiling-point.

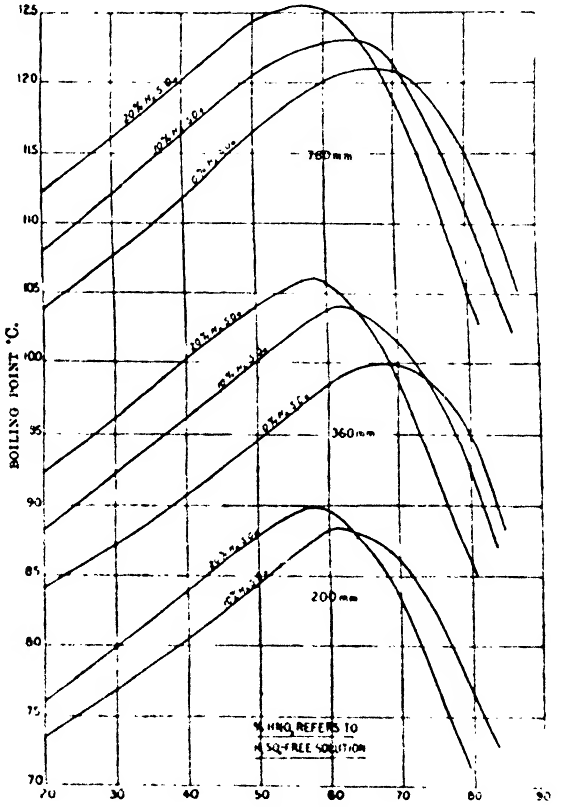

FIG. 125.—Influence of H_2SO_4 on the Boiling-points of Aqueous Nitric Acid.

Vapour Pressure.

Vapour pressure determinations of nitric acid and its solutions have been carried out by Saposchnikoff[2] and by Creighton and Githens.[3] The following graph, Fig. 126, is from data by the latter authors.

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[1] *J. Franklin Inst.*, 1915, **180**, 706.
[2] *Z. physik. Chem.*, 1905, **58**, 225.
[3] *J. Franklin Inst.*, 1915, **179**, 161-69.

Freezing-Point.

Küster and Münch give the melting-point of absolute nitric acid as −41° C.[1]

The freezing-points of aqueous solutions of nitric acid as obtained by Küster and Kremann[2] are given in Fig. 127.

Specific Heat.

The work of Pascal and Garnier[3] (see table below) is in general agreement with the earlier work of Marignac and Thomsen.

Per cent. HNO_3.	Per cent. NO_2.	Mean Specific Heat at 20°.
10·00	nil.	0·900
25·57	,,	0·787
40·00	,,	0·669
45·87	,,	0·662
60·52	,,	0·637
70·00	0·7	0·610
81·80	1·54	0·575
90·33	2·30	0·530
92·15	4·22	0·500
98·15	1·85	0·475

Vapour Density.

By mixing the vapour from nitric acid with dry air, Playfair and Wanklyn found the vapour density at 40·5° C. to be 34·3.[4]

The calculated value for HNO_3 is 31·5.

Heat of Solution.

The following table gives the results of determinations by Thomsen[5] and Berthelot[6] of the heat of solution in kilogram calories when 1 gram molecule of HNO_3 is dissolved in M. gram molecules of H_2O.

M.	0·5	1	1·5	2	2·5	3	4	5	6	8	10	20	40	80	100	160	200	320
Thomsen, 18° C. .	2·00	3·29	4·16	..	5·27	5·71	..	6·66	..	..	7·32	7·46	7·44	7·42	7·44	7·45	..	7·49
Berthelot, 10° C. .	2·08	3·34	4·16	4·86	..	5·76	6·39	6·76	6·98	7·22	7·27	7·30	7·27	..	7·21	..	7·18	..

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[1] *Z. anorg. Chem.*, 1905, **48**, 350.

[2] *Ibid.*, 1904, **41**, 1.

[3] *Bull. Soc. chim.*, 1920; [IV], **27**, 8-18.

[4] *J. Chem. Soc.*, 1862, **15**, 142.

[5] *Thermo. chem. Untersuch*, Leipzig, 1883, Bd. 3.

[6] *Ann. Chim. Phys.*, 1875, **5**, **4**, 468.

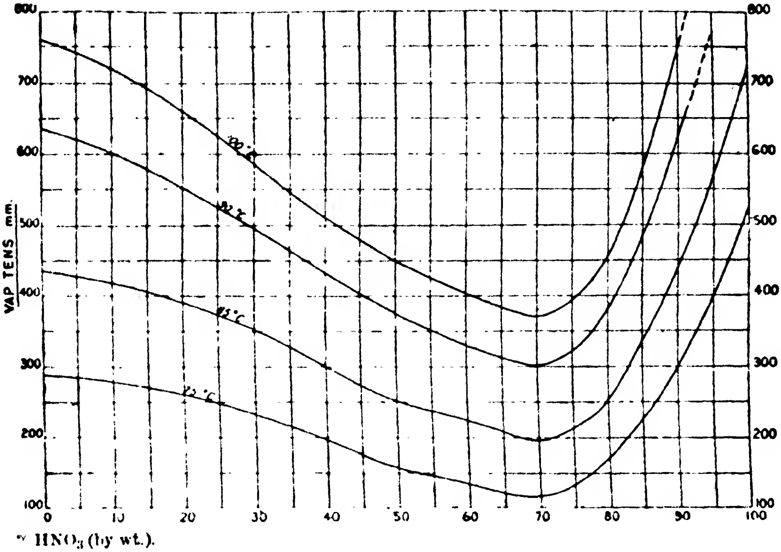

FIG. 126.—Vapour Tension of Aqueous Solutions of HNO_3 at different Temperatures.

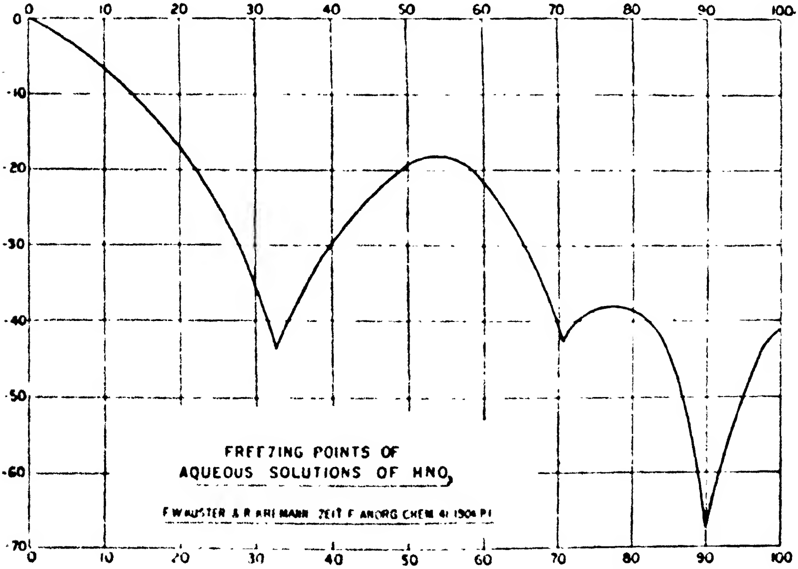

FIG. 127.

Hydrates.

Much investigation on the physical properties of nitric acid solutions has shown the existence of discontinuities in these properties pointing to the existence of various hydrates of nitric acid.

Veley and Manley, in a paper on "Some Physical Properties of Nitric Acid Solutions,"[1] point out that the physical properties of nitric acid display well-marked alterations at definite points, and that such points correspond very approximately to the concentrations required for simple molecular combinations *only* of nitric acid (HNO_3) with water.

Pickering succeeded in isolating two crystalline hydrates corresponding to

$HNO_3 . 3H_2O$ (53.7 per cent. HNO_3) Mp - 18° C.

(large fairly transparent crystals) and

$HNO_3 . H_2O$ (77.8 per cent. HNO_3) Mp - 36.8° C.

(smaller more opaque gritty crystals[2]).

Küster and Kremann also find the existence of the above hydrates.[3]

Electrical Conductivity.

From their work on the electrical conductivity of aqueous nitric acid solutions, Kohlrausch and Grotrian concluded that the conductivity increases with percentage concentration up to 30 to 33 per cent. HNO_3 and consequently decreases.[4]

The determinations of Veley and Manley show that the conductivity increases for percentage concentrations from 1·3 to 30 at first rapidly, then less rapidly; from this point the conductivity decreases slowly up to 70 per cent., thence more rapidly until a minimum is reached at 96·12 per cent. when a sudden increase takes place.[5]

The table on opposite page and curve (Fig. 128) on page 338 are from Veley and Manley's paper.

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[1] *Roy. Soc. Proc.*, **69**, 86-119.

[2] *J. Chem. Soc. Trans.*, 1893, **63**, 436.

[3] *Z. anorg. Chem.*, 1904, **41**, 1.

[4] *Ann. Phys. Chem.*, **154**, 215-39.

[5] *Phil. Trans.*, 1898, **191** A, 365-98.

Electrical Conductivities of Nitric Acid from 1·3 *per cent.* HNO_3 *to* 99·97 *per cent.* HNO_3 *at* 15° C.

Per cent. Concentration.	Specific Conductivities K × 10^8 Mercury Units.
1·30	632·06
3·12	1440·6
5·99	2618·1
10·13	4079·2
15·32	5460·5
20·11	6363·8
25·96	6875·7
30·42	7008·2
33·81	6962·8
35·90	6857·6
39·48	6648·5
45·01	6225·9
51·78	5554·2
53·03	5449·8
58·20	4908·8
61·20	4665·1
65·77	4060·3
69·53	3728·7
73·82	2877·0
76·59	2613·5
78·96	1945·1
84·08	1152·2
86·18	930·86
87·72	706·23
89·92	472·02
91·97	302·7
94·32	207·8
96·12	142·38
98·50	167·81
98·85	182·36
99·27	375·15
99·97	387·34

Magnetic Rotatory Power.

W. H. Perkin, senior, gives the following results for the magnetic rotatory power of nitric acid[1] :—

Molecular Composition.	Per cent. Composition.	Specific Rotation at 15° C.	Molecular Rotation.	Molecular Rotation less that due to H_2O.
HNO_3 + 0·019 H_2O	99·45	0·5292	1·226	1·207
+ 2·701 "	56·44	0·8042	3·678	0·977
+ 7·311 "	32·36	0·9066	8·163	0·852
+ 9·555 "	26·81	0·9238	10·360	0·805
+ 12·030 "	22·54	0·9350	12·783	0·753

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[1] *J. Chem. Soc. Trans.*, 1893, **63**, 65.

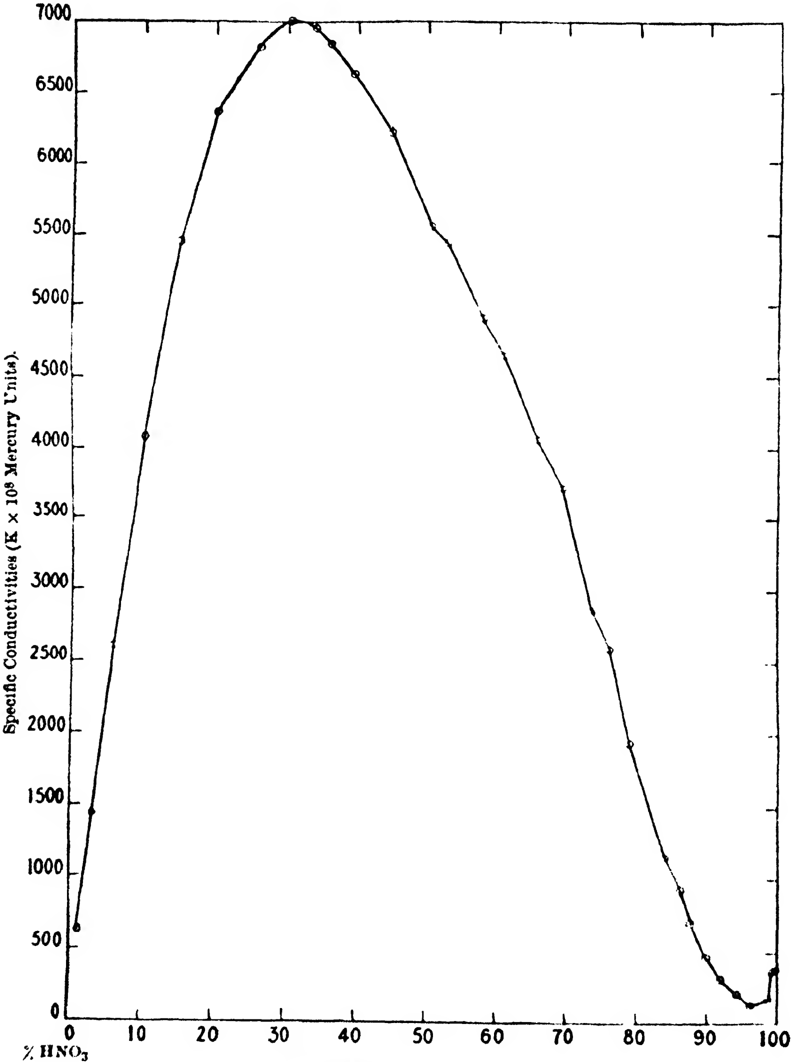

Fig. 128.—Electrical Conductivities of Nitric Acid.

Refractive Index.

According to Veley and Manley, values for μ_D increase slowly with increase of percentage of HNO_3 to 70 per cent., where the maximum value is reached; from this point the values decrease to 98·67 per cent. and then there is a slight increase. The refractive index for the anhydrous acid is approximately equal to that of an acid of 50 per cent. HNO_3.[1]

The accompanying table is from the paper by Veley and Manley:—

Refractive Indices at 14·2° C.[2]

Percentage Concentration.	$\mu_D^{14\cdot2}$	Percentage Concentration.	$\mu_D^{14\cdot2}$	Percentage Concentration	$\mu_D^{14\cdot2}$
2·19	1·336208	41·45	1·388788	75·23	1·405599
3·85	·338434	44·69	·392305	78·07	·405091
6·76	·342298	46·90	·394496	81·12	·404504
9·29	·345824	49·12	·396699	84·11	·403427
11·88	·349371	50·00	·398435	85·80	·402924
16·11	·355107	54·63	·401017	87·20	·402412
18·27	·358541	57·00	·402440	89·88	·401419
21·66	·363091	60·33	·404080	91·29	·401017
25·07	·365152	63·07	·405157	92·82	·400249
29·40	·374225	66·60	·405860	95·66	·398148
32·60	·377798	67·92	·405985	98·67	·396980
34·26	·380354	70·04	·406094	99·87	·397167
36·68	·383039	71·57	·406046	. .	...
39·11	·386262	74·63	·405696	...	..

Absorption Spectra.

The absorption spectra of nitric acid and its solutions have been studied by Hartley.[3]

Viscosity.

The following values for viscosities of nitric acid solutions are given by Küster and Kremann[4]:—

Per cent. HNO_3 .	98·5	82·0	70·0	65·0	50·0	30·0	10·0	0
η (+15° C.) . .	0·548	1·036	1·277	1·300	1·144	0·822	0·655	...
η (−15° C.) . .	0·833	2·240	3·268	3·304	2·369	1·635	...	...

η = 1 for water at 0° C.

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[1] *Roy. Soc. Proc.*, **69**, 86-119.

[2] Veley and Manley, *Roy. Soc. Proc.*, **69**, 114.

[3] *J. Chem. Soc. Trans.*, 1903, **83**, 658-66; *ibid.*, p. 233.

[4] *Z. anorg. Chem.*, 1904, **41**, 13.

Latent Heat of Fusion and Evaporation.[1]

	Gram Calories per 1 gram.	Gram Calories per 1 gram Molecule.
Latent Heat of Fusion. .	9·54	601
Latent Heat of Evaporation	115·1	7250

Heat of Formation.

$$H + N + O_3 + Aq = HNO_3\ Aq + 49{,}090 \text{ cals. Thomsen.}$$
$$+ 48{,}800 \text{ cals. Berthelot.}$$

whence by subtracting the heat of solution—

7490 Thomsen
7180 Berthelot

we get—

$$H + N + O_3 = HNO_3 + 41{,}600 \text{ cals. (gram calories).}$$

$(NO_3)'$ Ion.

The nitrate $(NO_3)'$ ion is one of the most electro-negative ions, and its absolute velocity at 18° under a potential gradient of 1 volt per cm. is $6{\cdot}4 \times 10^{-4}$ cms. per second.[2]

Nitric acid is very highly ionised in dilute solution and by the usual methods of comparison (*e.g.*, by avidity, inversion of cane sugar, hydrolysis of methyl acetate, electrical conductivity, etc.); it is the second strongest acid, being preceded only by hydrochloric acid.

Heat of Neutralisation.

The heat of neutralisation of nitric acid with sodium hydroxide is 13,680 cals., and with potassium hydroxide 13,770 cals.[3]

Molecular Weight.

The molecular weight of nitric acid is 63·02.

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[1] Berthelot, *Ann. Chim. Phys.*, 1877; [V], 12, 530.

[2] M'Lewis, *A System of Physical Chemistry*, 1920, vol. i., p. 212.

[3] Thomsen, *Th. Untersuch*, 1906, p. 40.

Constitution of Concentrated Acid.

The purest concentrated nitric acid behaves very differently from the normally obtained concentrated acid. Veley and Manley found that acid of 99·97 per cent. HNO_3 had no action on copper, silver, cadmium, or mercury, of a high degree of purity, nor on commercial magnesium at ordinary temperature; purified iron and commercial zinc were not affected by the acid even when boiling. Purified zinc was slightly acted on, while sodium immediately caught fire. The acid had no action whatever on calcium carbonate at ordinary temperature or at the boiling-point.[1]

Aston and Ramsay found that nitric acid in the liquid state has a molecular weight greater than that expressed by the formula HNO_3, and suggested that it probably consists of a large proportion of molecules of $H_2N_2O_6$ mixed with simple molecules.[2]

From his work on absorption spectra, Hartley concluded that in all probability nitric acid is more or less of the nature $\eta(HNO_3)$.[3]

FUMING NITRIC ACID.

Preparation.

Fuming nitric acid is a concentrated nitric acid containing variable quantities of N_2O_4 in solution. It is a red fuming liquid produced by adding nitrous acid, nitrous anhydride, nitrogen peroxide, or nitric oxide to concentrated nitric acid.

It is also obtained by distilling sodium or potassium nitrate with half its weight of sulphuric acid, when in the second stage of the reaction the decomposition represented by the equation

$$KHSO_4 + KNO_3 = K_2SO_4 + HNO_3$$

takes place at so high a temperature that part of the nitric acid is decomposed with formation of NO_2 which dissolves in the distillate.

By distilling concentrated nitric acid with concentrated

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[1] *Phil. Trans.*, 1898, **191** A, 365.

[2] *J. Chem. Soc.*, 1894, **65**, 169.

[3] *J. Chem. Soc. Trans.*, 1903, **83**, 658.

sulphuric acid, the latter partially dehydrates the nitric acid, and nitrogen peroxide, which results, dissolves in the distillate.

By introducing into the distilling mixture of sodium or potassium nitrate and sulphuric acid a quantity of starch, reduction of a portion of the nitric acid formed takes place, and the resulting nitrogen peroxide dissolves in the unreduced nitric acid.

Fuming nitric acid may also be obtained by adding paraformaldehyde to concentrated nitric acid.[1]

In any case the distillate should be caught in a well-cooled receiver to prevent loss of nitrogen peroxide.

It is obtained commercially where partial decomposition of nitric acid has been brought about by the presence of organic matter, by heat or other means.

Properties.

It is dark red in colour, fumes strongly in the air, and is a more active oxidising agent than pure nitric acid.

On dilution with water the fuming acid changes in colour from dark red through browns to yellowish green. With ice-cold water a dilute solution is blue.

The green solutions contain HNO_2 and N_2O_4, whilst the blue solutions contain only HNO_2.[2]

The specific gravities of fuming acid of different N_2O_4 contents are given on p. 328.

AQUA REGIA.

The preparation of this active reagent was first recorded by Geber in the eighth century, who prepared it by dissolving sal ammoniac in aqua fortis and recognised its power of dissolving gold. The name aqua regia is first found, according to Roscoe, in the writings of Basil Valentine, who prepared it by the method given by Geber, and also by mixing nitric and hydrochloric acids.

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[1] Vanino, *Ber.*, 1899, **32**, 1392-3.

[2] Marchlewski, *Z. anorg. Chem.*, 1892, **1**, 368, and 1892, **2**, 18; with Liljernstein, 1894, **5**, 288.

It is obtained when nitric and hyrochloric acids are mixed in the ratio of one of the former to three of the latter.

$$HNO_3 + 3HCl = NOCl + Cl_2 + H_2O.$$

Its solvent power depends on the presence of free chlorine in solution.

Chemical Properties of Nitric Acid.

General.

Nitric acid is extremely corrosive and causes painful wounds on the skin (see p. 186). Its action on organic matter is rapid, being partly oxidising and partly nitrating with formation of nitric esters or nitro-substitution bodies. Dilute solutions give a bright yellow coloration with skin, hair, wool, etc.

Nitric acid is extremely reactive, being a very energetic oxidising agent. Acting as an oxidising agent it is itself reduced, and the nature of the reduction product is dependent on many factors. Some of the recognised reduction products of nitric acid are, NO_2, HNO_2, N_2O_3, NO, N_2O, N_2, NH_2OH, and NH_3.

Reactions.

1. Carius has shown that nitric acid is completely decomposed by heat at about 256° C., according to the equation

$$4HNO_3 = 4NO_2 + 2H_2O + O_2.$$

The following table, giving results obtained by Carius,[1] shows the extent of decomposition at various temperatures:—

Temperature of Decomposition.	S.G. of Vapour.		Percentage Decomposition.	Oxygen from 1 gram HNO_3.
	Air = 1.	H = 1.		
86° C.	2·05	29·6	9·53	8·43 c c.
100	2·02	29·1	11·77	10·41 ,,
130	1·92	27·6	18·78	16·62 ,,
160	1·79	25·8	28·96	26·22 ,,
190	1·59	23·0	49·34	43·69 ,,
220	1·42	20·4	72·07	63·77 ,,
250	1·29	18·6	93·03	82·30 ,,
256	1·25	18·0	100·00	88·47 ,,
265	1·24	17·9	...	...
312	1·23	17·8	...	...

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[1] L. Carius, *Ber.* [IV], 828-34.

2. Concentrated nitric acid is slowly decomposed at the ordinary temperature on exposure to sunlight, giving nitrogen peroxide, water, and oxygen, so that on standing exposed to sunlight the acid becomes yellow and contains N_2O_4.

$$4HNO_3 = 2N_2O_4 + 2H_2O + O_2.$$

According to Berthelot this reaction is endothermic and not entirely reversible and does not take place with dilute acid. Acid of sp. gr. 1·365, corresponding to the composition $HNO_3 . 2\frac{1}{2}H_2O$, was found to have undergone no appreciable amount of decomposition after several weeks' exposure.[1]

The products of decomposition slowly recombine more or less completely in the absence of light.[2]

Veley and Manley suggest that the decomposition in sunlight is a decomposition of the vapour rather than of the liquid.[3]

3. Nitric acid may be completely decomposed by passing the vapour over highly incandescent copper, since the oxides of nitrogen first formed give up their oxygen to the copper so that only water and nitrogen remain.

4. Berthelot showed that at ordinary temperatures and at 100° C., free hydrogen exerts no decomposing action on nitric acid.[4]

Hydrogen evolved in presence of nitric acid reduces the acid, giving reduction products which vary with the concentration. This reducing effect is seen during the electrolysis of solutions of nitric acid, when the hydrogen which is liberated from the cathode causes the production of nitrous acid, N_2O_3, NO, N_2, and NH_3, according to the conditions.

With very dilute solutions the hydrogen evolved does not sensibly affect the nitric acid.[5] Concentrated nitric acid is rapidly reduced by hydrogen occluded by Pt or Pd.[6]

5. **Nitric Acid and the Metals.**—Gold, platinum, iridium, tantalum, rhodium, and titanium do not react with nitric acid.

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[1] *Comptes rend.*, 1898, **127**, 143.

[2] Reynolds and Taylor, *J. Chem. Soc. Proc.*, 1911, **27**, 306; *J. Chem. Soc. Trans.*, 1912, **101**, 131.

[3] *Phil. Trans.*, 1898, **191** A, 367.

[4] *Comptes rend.*, **127**; [I], 27-29.

[5] See Bourgoin, *J. Pharm.*, 1871; [IV], **18**, 266; Gladstone and Tribe, *J. Chem. Soc.*, 1879, **35**, 173.

[6] Gladstone and Tribe, *ibid.*; Banerjee and Banerjee, *J. Chem. Soc. Proc.*, 1911, **27**, 326.

On adding magnesium to very dilute nitric acid (one of acid to six or eight of water), hydrogen is evolved along with nitrous and nitric oxides and nitrogen.[1] In the cold the hydrogen evolved is nearly pure. As the solution becomes warm and the percentage of magnesium nitrate increases, the production of hydrogen rapidly diminishes.[2]

The metals which react with nitric acid cause decomposition of the acid and at the same time go into solution as nitrates, though in some cases the nitrates first produced are decomposed with the final production of hydrated oxides, *e.g.*, with tin, antimony, arsenic, tungsten, and molybdenum.

The question as to exactly what happens when various metals react with nitric acid has proved a very vexed one. Apart from the intrinsic complexity of the reduction of nitric acid, the question has been further complicated owing to the uncertainties as regards impurity factors which have come into play during the many investigations.

The reduction products resulting from the action of metals on nitric acid vary with temperature and concentration of acid, with the nature of the metal, and with the accumulation in the solution of reduction and solution products of the reaction.

Divers[3] divides the metals into two classes as regards their action on nitric acid. Silver, mercury, copper, and bismuth form one class, and result in the primary formation of nitrite and nitrate with subsequent secondary formation of nitrous acid, nitric oxide, and nitrogen peroxide. He considers nitrous acid necessary for the reaction, but only as a catalyst and not as influencing the accumulating quantity of nitrite.

The reaction with silver is represented as follows:—

$$(1)\quad 2\,Ag + 2HNO_3 = \underbrace{AgNO_2 + AgNO_3 + H_2O}_{\text{primary products}}$$

$$\left.\begin{array}{lll} & (2) & AgNO_2+HNO_3 = AgNO_3+\underline{HNO_2} \\ \text{But} & (3) & HNO_2+HNO_3 \rightleftarrows \underline{2NO_2}+H_2O \\ \text{and} & (4) & 3HNO_2 \rightleftarrows HNO_3 + \underline{2NO}+H_2O \end{array}\right\}\begin{array}{l}\text{secondary}\\ \quad\text{reactions.}\end{array}$$

Reaction (2) occurs (*a*) when there is not sufficient nitrous acid present to act as a catalyst; and (*b*) when there is not

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[1] Gladstone and Tribe, *J. Chem. Soc.*, 1879, **35**, 178-9.

[2] Ewart, *Pharm. J.*, 1902, **68** ; [1649], 82 ; *Nature*, **65**, 128.

[3] *J. Chem. Soc. Trans.*, 1883, **43**, 443-66.

sufficient water present to preserve the nitrite from the action of nitric acid.

Reaction (3) occurs with concentrated acid.

Reaction (4) occurs with dilute acid.

The second class includes aluminium, cadmium, iron magnesium, lead, tin, zinc, and the alkali metals. The primary products in this case are nitrate and hydroxylamine. As secondary products ammonia, nitrogen, nitrous oxide, nitric oxide and nitrogen peroxide appear independently of each other without intermediate production, and nitrite and nitrous acid are formed by the action of the metals on their own nitrates.

These two broad class divisions of the metals coincide with their classification in the potential series, the electro-positive metals behaving differently from those which are electro-negative.

The influence of nitrous acid on the activity of nitric acid on metals was first noticed by Millon,[1] while Veley showed that nitric acid quite free from nitrous acid had no action on ordinarily reactive metals.[2]

Banerjee and Banerjee[3] favour the nascent hydrogen theory in explanation of the action of nitric acid on metals, and uphold the view of Montemartini that those metals which decompose water at a high temperature give with nitric acid, N_2O_4, N_2O_3 and NO; whilst those which decompose water at a low temperature give in addition to the above, N_2O, N_2 and NH_3; and those decomposing water at the ordinary temperature also evolve hydrogen.

Freer and Higley[4] have measured the relative amounts of the reduction products when iron dissolves in nitric acid of different concentrations. Their results show that the degree of reduction decreases with increase of acid concentration, and whilst a large percentage of ammonia is formed with very weak acid, only nitrogen peroxide is formed with very strong acid.

According to Veley and Manley, nitric acid containing

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[1] *J. Pharm. Chim.*, 1842; [III], 2, 179.

[2] *J. Soc. Chem. Ind.*, 1891, **10**, 204.

[3] *J. Chem. Soc. Proc.*, 1911, **27**, 326.

[4] *Amer. Chem. J.*, 1899, **21**, 377-92.

99·97 per cent. HNO_3 has no action on copper, silver, cadmium, or mercury, or on commercial magnesium at ordinary temperatures; purified iron and commercial granulated zinc were not affected by the acid even when boiling; purified zinc was slightly acted on; sodium immediately caught fire. The acid had no action whatever on calcium carbonate at ordinary temperatures or the boiling-point. Flowers of sulphur and ferrous sulphide dissolved quickly in the gently warmed acid.[1]

Concentrated nitric acid causes iron to assume the "passive" state so that the surface of the metal is rendered inactive and is no longer acted upon by dilute nitric acid, which previously dissolved it freely.

All except the very active metals may be rendered passive by making them the anode in a nitric acid solution and increasing the current density. At a definite current density dissolution ceases, and thereafter the anode behaves like a noble metal anode, oxygen being evolved.

It is considered that passivity is probably due to some form of association of oxygen with the metal at its surface.

6. All the solid non-metals are oxidised by nitric acid, with consequent reduction of the latter.[2]

e.g.

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$$
$$S + 2HNO_3 = H_2SO_4 + 2NO$$
$$6P + 10HNO_3 + 4H_2O = 6H_3PO_4 + 10NO$$

Nitric acid is used in quantitative organic analysis for oxidation of the sulphur in sulphur-containing compounds to sulphuric acid and of phosphorus to phosphoric acid, which are then estimated gravimetrically. The method is due to Carius.

7. Compounds in a lower state of oxidation are further oxidised by nitric acid.

e.g. ferrous salts are oxidised to ferric
stannous salts are oxidised to stannic, etc.

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$
$$SnCl_2 + 2HCl + 2HNO_3 = SnCl_4 + 2NO_2 + 2H_2O.$$

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[1] *Phil. Trans.*, 1898, **191** A, 365.

[2] Montemartini, *Gazz. Chim. Ital.*, 1898; [I], **28**, 397.

Sulphur dioxide is oxidised by concentrated nitric acid forming sulphuric acid and nitrogen peroxide—

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$$

With more dilute nitric acid, the nitric acid is reduced to nitric oxide—

$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO$$

Nitric acid vapour and SO_2 form nitro-sulphonic acid NO_2, SO_2, OH.

8. Sulphides may give nitrates and sulphuretted hydrogen, but the latter compound is further oxidised to sulphur and then to sulphuric acid, with formation of metallic sulphates.

e.g.

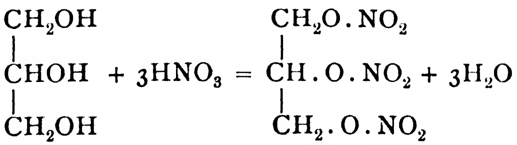
$$\begin{array}{lll} (1) & PbS + 2HNO_3 & = Pb(NO_3)_2 + H_2S \\ (2) & 3PbS + 8HNO_3 & = 3Pb(NO_3)_2 + 4H_2O + 3S + 2NO \\ (3) & 3PbS + 14HNO_3 & = 3Pb(NO_3)_2 + 4H_2O + 3H_2SO_4 + 8NO \end{array}$$

9. Hydriodic acid and iodides are oxidised, giving iodine and water with consequent reduction of the nitric acid to NO.

Hydrobromic acid at 0° forms Br_2 and NO_2.

Hydrochloric acid gives H_2O, NOCl, and Cl_2 (see Aqua Regia, p. 342).

10. Organic compounds behave very differently with nitric acid according to their nature. With aliphatic compounds the general tendency of nitric acid is to oxidise the carbon compound, but characteristic nitrate formations are exemplified in the production of nitro-glycerine and nitro-cotton. In the formation of such nitrates the group $-NO_2$ replaces H of the OH radicle, *e.g.*:—

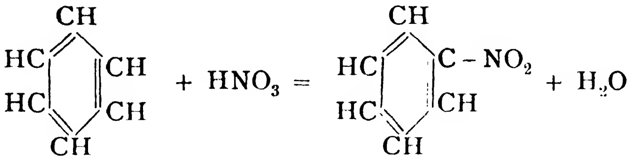


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HNO_3 = \begin{array}{l} CH_2O.NO_2 \\ | \\ CH.O.NO_2 \\ | \\ CH_2.O.NO_2 \end{array} + 3H_2O$$

Glycerine. Nitro-glycerine.

With aromatic compounds, nitric acid reacts to produce a class of bodies known as nitro-compounds, in which the

$-NO_2$ group replaces H which was directly attached to carbon, *e.g.*:—



$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$

Benzene. Nitro-benzene.

In oxidising such bodies as hay, straw, and sawdust, concentrated nitric acid readily causes them to inflame.

Starch decomposes nitric acid with production of NO, NO_2, and N_2O_3.

Nitric acid is a mono-basic acid and forms a series of salts called nitrates which are specially characterised by nearly all being easily soluble in water, from solutions in which they usually crystallise well. They may be obtained by neutralising the acid with the oxide or carbonate of the metal, though usually they may be prepared by dissolving the metal in nitric acid.

Only in rare instances are acid or basic nitrates obtained. Bismuth and mercuric nitrates are hydrolysed in water, giving basic nitrates which are insoluble in water but which dissolve in dilute nitric acid.

$$\textit{e.g.}\quad Bi(NO_3)_2 + 2H_2O \rightleftarrows BiNO_3(OH)_2 + 2HNO_3$$

Nitrates are all capable of evolving oxygen when heated, and therefore act as oxidising agents.

$$\textit{e.g.}\quad 2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$
$$2KNO_3 = 2KNO_2 + O_2$$

REFERENCES.

Historical.

PRIESTLEY.—"Observations on Different Kinds of Air.'
LAVOISIER.—Lavoisier, *Œuvres*; [II], 226.
CAVENDISH.—*Phil. Trans.*, 1784, p. 119; 1785, p. 372.
RAYLEIGH.—*J. Chem. Soc.*, 1897, **71**, 181.

Occurrence.

WARRINGTON.—*J. Chem. Soc. Trans.*, 1889, **55**, 537.

Formation.

By Burning Hydrogen in the Air, or in Oxygen in the Presence of Nitrogen.

Hofmann.—*Ber.*, 1870, **3**, 663.

Lavoisier.—Lavoisier, *Œuvres*; [II], 226.

Cavendish.—*Phil. Trans.*, 1784-5.

Bunsen.—*Gasometry*, 1857, p. 58.

Kolbe.—*Annalen*, **119**, 176.

M. Berthelot.—*Comptes rend.*, 1900, **130**, 1345-53; *J. Chem. Soc. Abstr.*, 1900; [II], **78**, 475; *Comptes rend.*, 1900, **130**, 1662-77; *J. Chem. Soc. Abstr.*, 1900; [II], **78**, 538.

By Combustion of Coal-Gas in Air.

L. T. Wright.—*J. Chem. Soc. Trans.*, 1879, **35**, 42-6.

Ilosva.—*Bull. Soc. chim.*, 1889; [III], **2**, 736.

By Passing Electric Sparks through a Mixture of Moist Nitrogen and Oxygen.

F. von Lepel.—*Ber.*, 1903, **36**, 1251-8; *J. Chem. Soc. Abstr.*, 1903; [II], **84**, 420.

G. Meyer.—*Z. physik. Chem. Unter.*, 1908, **21**, 40; *J. Chem. Soc. Abstr.*, 1908; [II], **94**, 487.

A. Makowetzky.—*Z. Elektrochem.*, 1911, **17**, 217-35; *J. Chem. Soc. Abstr.*, 1911; [II], **100**, 463.

By Silent Discharge.

M. Berthelot.—*Comptes rend.*, 1906, **142**, 1367-79; *J. Chem. Soc. Abstr.*, 1906; [II], **90**, 533.

By Nitrifying Bacteria.

Adeney.—*Trans. Roy. Soc., Dublin*, 1897; [II], **6**, 269-81; *J. Chem. Soc. Abstr.*, 1898; [II], **74**, 86.

Murmann.—*Oesterr. Chem. Zeit.*, 1907; [II], **10**, 181; *J. Chem. Soc. Abstr.*, 1907; [II], **92**, 905.

Pure Acid.

Roscoe.—*J. Chem. Soc. Trans.*, 1861, **13**, 150.

G. Lunge and H. Rey.—*Z. angew. Chem.*, 1891, p. 165.

V. H. Veley and J. J. Manley.—*Phil. Trans.*, 1898, **191** A, 368-72; 386-88.

Kolb.—*Ann. Chim. Phys.*; [IV], **10**, 140.

F. W. Küster and S. Münch.—*Z. anorg. Chem.*, 1905, **43**, 350.

O. Silberrad and B. J. Smart.—*J. Soc. Chem. Ind.*, 1906, **25**, 156.

K. Schaeffer and H. Niggemann.—*Z. anorg. Chem.*, 1916, **97**, 285-311; *J. Chem. Soc. Abstr.*, 1917; [II], **112**, 61.

Krumenacher.—*Schweiz. Chem. Zeit.*, 1917, **1**, 116-20; *J. Chem. Soc. Abstr.*, 1918; [II], **114**, 438.

Pascal and Garnier.—*Bull. Soc. chim.*, 1919; [IV], **23**, 312.

Physical Properties.

APPEARANCE.

L. Marchlewski.—*Ber.*, **24**, 3271-6 ; *J. Chem. Soc. Abstr.*, 1892, **62**, 113.
Aston and Ramsay.—*J. Chem. Soc. Trans.*, 1894, **65**, 169.
F. W. Küster and S. Münch.—*Z. anorg. Chem.*, 1905, **48**, 350-5 ; *J. Chem. Soc. Abstr.*, 1905 ; [II], **88**, 243.

SPECIFIC GRAVITY.

Kirwan.—*Irish Acad. Trans.*, 1790, **4**, 3.
Ure.—*Quart. Journ. Sci.*, 1818, **4**, 291.
Kolb.—*Ann. Chim. Phys.* ; [IV], **10**, 140.
G. Lunge and H. Rey.—*Z. angew. Chem.*, 1891, pp. 165-70 ; *J. Chem. Soc. Abstr.*, 1892, **62**, 13.
G. Lunge and Marchlewski.—*Z. angew. Chem.*, 1892, **10-12**, 330-1 ; *J. Chem. Soc. Abstr.*, 1893 ; [II], **64**, 66.
Veley and Manley.—*J. Soc. Chem. Ind.*, 1903, **22**, 1227-9 ; *J. Chem. Soc. Trans.*, 1903, **83**, 1016.
F. Winteler.—*Chem. Zeit.*, 1905, **29**, 689 ; *J. Chem. Soc. Abstr.*, 1905 ; [II], **88**, 553.
G. Lunge.—*Chem. Zeit.*, 1905, **29**, 933-4 ; *J. Chem. Soc. Abstr.*, 1905, **88**, 651.
W. C. Ferguson.—*J. Soc. Chem. Ind.*, 1905, **24**, 781.
W. R. Bousfield.—*J. Chem. Soc. Trans.*, 1915, **107**, 1407.
Pascal and Garnier.—*Bull. Soc. chim.*, 1919 ; [IV], **25**, 312 ; *J. Chem. Soc. Abstr.*, 1919 ; [II], **116**, 339.

BOILING-POINT.

J. M. Creighton and J. H. Githens.—*J. Franklin Inst.*, 1915, **179**, 161-9 ; *J. Chem. Soc. Abstr.*, 1915 ; [II], **108**, 446.
J. M. Creighton and Smith.—*J. Franklin Inst.*, 1915, **180**, 703-9 ; *J. Chem. Soc. Abstr.*, 1916 ; [II], **110**, 97.
P. Pascal.—*Comptes rend.*, 1917, **165**, 589-91 ; *J. Chem. Soc. Abstr.*, 1917 ; [II], **112**, 569 ; *Bull. Soc. chim.*, 1920 ; [IV], **27**, 814-20 ; *J. Chem. Soc. Abstr.*, 1920 ; [II], **117**, 752.
J. Baumann.—*Chem. Zeit.*, 1920, **44**, 678 ; *J. Chem. Soc. Abstr.*, 1920 ; [II], **117**, 686.

CONSTANT BOILING-POINT.

Roscoe.—*J. Chem. Soc. Trans.*, 1861, **13**, 146.
Smith.—*Phil. Mag.* ; [III], **31**, 454.
J. M. Creighton and Smith.—*J. Franklin Inst.*, 1915, **180**, 703-9 ; *J. Chem. Soc. Abstr.*, 1916 ; [II], **110**, 97.
J. Baumann.—*Chem. Zeit.*, 1920, **44**, 678 ; *J. Chem. Soc. Abstr.*, 1920 ; [II], **117**, 686.

VAPOUR PRESSURE.

Saposchnikoff.—*Z. physik. Chem.*, 1905, **53**, 225.
Creighton and Githens.—*J. Franklin Inst.*, 1915, **179**, 161-9 ; *J. Chem. Soc. Abstr.*, 1915 ; [II], **108**, 446.

C. L. BURDICK AND E. S. FREED.—*J. Amer. Chem. Soc.*, 1921, **43**, 518; *J. Chem. Soc. Abstr.*, 1921; [II], **120**, 313.

FREEZING-POINT.

PICKERING.—*J. Chem. Soc. Trans.*, 1893, **63**, 436-43.
H. C. JONES.—*Z. physik. Chem.*, 1893, **12**, 630.
H. C. JONES AND F. H. GETMAN.—*Amer. Chem. J.*, 1902, **27**, 433-44; *J. Chem. Soc. Abstr.*, 1902; [II], **82**, 489.
KÜSTER AND KREMANN.—*Z. anorg. Chem.*, 1904, **41**, 1-42; *J. Chem. Soc. Abstr.*, 1904; [II], **86**, 726.
KÜSTER AND MÜNCH.—*Z. anorg. Chem.*, 1905, **43**, 350-5; *J. Chem. Soc. Abstr.*, 1905; [II], **88**, 243.

SPECIFIC HEAT.

PASCAL AND GARNIER.—*Bull. Soc. chim.*, 1920; [IV], **27**, 8-18; *J. Chem. Soc. Abstr.*, 1920; [II], **118**, 162.
W. RICHARDS AND A. W. ROWE.—*J. Amer. Chem. Soc.*, 1921, **43**, 770-96.

VAPOUR DENSITY.

PLAYFAIR AND WANKLYN.—*J. Chem. Soc.*, 1862, **15**, 142.

HEATS OF SOLUTION.

BERTHELOT.—*Ann. Chim. Phys.*, 1875, **5**, **4**, 468.
THOMSEN.—*Thermo. Chem. Untersuch.*, Leipzig, 1883, Bd. **3**.

CONTRACTION ON MIXING.

KOLB.—*Ann. Chim. Phys.*; [IV], **10**, 136.
VELEY AND MANLEY.—*Roy. Soc. Proc.*, **69**, 86-119; *J. Chem. Soc. Abstr.*, 1902; [II], **82**, 135.

HYDRATES.

MENDELEJEFF.—3rd Eng. Edit., **1**, 290-1, note 34.
BERTHELOT.—*Mécanique Chimique*, **2**, 157.
THOMSEN.—*Thermo. Chem. Untersuch.*, **3**, 66.
E. BOURGOIN.—*J. Pharm. Chim.*; [IV], **13**, 266; *J. Chem. Soc. Abstr.*, 1871, **9**, 885.
R. WEBER.—*Pogg. Ann.*, **147**, 113-28; *J. Chem. Soc. Abstr.*, 1872, **10**, 1072.
KOLB.—*Ann. Chim. Phys.*; [IV], **10**, 136.
H. CROMPTON.—*J. Chem. Soc. Trans.*, 1888, **53**, 121.
W. H. PERKIN (senior).—*J. Chem. Soc. Trans.*, 1889, **55**, 724.
VOLNEY.—*J. Amer. Chem. Soc.*, 1891, **13**, 246.
PICKERING.—*J. Chem. Soc. Trans.*, 1893, **63**, 436-43.
VELEY.—*Ber.*, 1895, **28**, 928-31; *J. Chem. Soc. Abstr.*, 1895; [II], **68**, 262.
VELEY AND MANLEY.—*Phil. Trans.*, 1898, **191 A**, 365-98; *J. Chem. Soc. Abstr.*, 1898; [II], **74**, 277; *Roy. Soc. Proc.*, **69**, 86-119; *J. Chem. Soc. Abstr.*, 1902; [II], **82**, 135.

H. Erdmann.—*Z. anorg. Chem.*, 1902, **32**, 431-6; *J. Chem. Soc. Abstr.*, 1903; [II], **84**, 73; *Z. angew. Chem.*, 1903, **16**, 1001; *J. Chem. Soc. Abstr.*, 1904; [II], **86**, 26.

Veley and Manley.—*J. Chem. Soc. Trans.*, 1903, **83**, 1015-21.

Hartley.—*Ibid.*, pp. 658-66.

F. W. Küster.—*Z. angew. Chem.*, 1903, **16**, 1079-80; *J. Chem. Soc. Abstr.*, 1904; [II], **86**, 26.

F. W. Küster and R. Kremann.—*Z. anorg. Chem.*, 1904, **41**, 1-42; *J. Chem. Soc. Abstr.*, 1904; [II], **86**, 726.

W. N. Hartley.—*Roy. Soc. Proc., Dublin*, 1905; [II], **10**, 373-7; *J. Chem. Soc. Abstr.*, 1905; [II], **88**, 815.

W. R. Bousfield.—*J. Chem. Soc. Trans.*, 1915, **107**, 1405-21.

Berl and Samtleben.—*Z. angew. Chem.*, 1922, **35**, 201-2, 206-11.

Electrical Conductivity.

Kohlrausch and Grotrian.—*Ann. Phys. Chem.*, **154**, 215-39.

Ostwald.—*J. prakt. Chem.*, **30**, 228; **31**, 437; *Z. physik. Chem.*, **1**, 75.

Bouty.—*Comptes rend.*, **106**, 595.

Kohlrausch.—*Wied. Ann.*, 1885, **26**, 161.

Arrhenius.—*Z. physik. Chem.*, 1887, **1**, 75; 1889, **4**, 96.

Loomis.—*Ann. Phys. Chem.*, 1897; [II], **60**, 547-51; *J. Chem. Soc. Abstr.*, 1897; [II], **72**, 301.

Veley and Manley.—*Phil. Trans.*, 1898, **191A**, 365-98; *J. Chem. Soc. Abstr.*, 1898; [II], **74**, 277.

F. W. Küster and R. Kremann.—*Z. anorg. Chem.*, 1904, **41**, 1-42; *J. Chem. Soc. Abstr.*, 1904; [II], **86**, 726-7.

E. C. C. Baly, K. A. Burke, and E. G. Marsden.—*J. Chem. Soc. Trans.*, 1909, **95**, 1103.

Jones and Getman.—*Amer. Chem. J.*, 1902, **27**, 433-44; *J. Chem. Soc. Abstr.*, 1902; [II] **82**, 489.

Magnetic Rotatory Power.

W. H. Perkin (senior).—*J. Chem. Soc. Trans.*, 1893, **63**, 57-75.

Refractive Index.

Baden Powell.—*The Undulatory Theory*, London, 1841, p. 112.

Van der Willigen.—*Archives Musée Teyler*, Haarlem, 1868; (I), 79; 1869; (II), 238.

Gladstone.—*Roy. Soc. Proc.*, **16**, 439; *Phil. Trans.*, 1870; *J. Chem. Soc. Trans.*, 1891, **59**, 589.

J. H. Gladstone and W. Hibbert.—*J. Chem. Soc. Trans.*, 1895, **67**, 831.

J. H. Gladstone and W. Hibbert.—*J. Chem. Soc. Trans.*, 1897, **71**, 828.

J. W. Brühl.—*Z. physik. Chem.*, 1897, **22**, 373; *J. Chem. Soc. Abstr.*, 1897; [II], **72**, 297.

Veley and Manley.—*Roy. Soc. Proc.*, **69**, 86-119; *J. Chem. Soc. Abstr.*, 1902; [II], **82**, 135; *J. Chem. Soc. Trans.*, 1903, **83**, 1019.

Absorption Spectra.

Hartley.—*J. Chem. Soc. Trans.*, 1903, **88**, 233 ; *ibid.*, pp. 658-66.

E. C. C. Baly, K. A. Burke, and E. A. Marsden.—*J. Chem. Soc. Trans.*, 1909, **95**, 1103.

K. Schaeffer and H. Niggemann.—*Z. anorg. Chem.*, 1916, **97**, 285-311 ; *J. Chem. Soc. Abstr.*, 1917 ; [II], **112**, 61.

Viscosity.

Graham.—*Phil. Trans.*, 1861, **153**, 373-5.

Reyher.—*Z. physik. Chem.*, 1888, **2**, 744.

Küster and Kremann.—*Z. anorg. Chem.*, 1904, **41**, 1-42 ; *J. Chem. Soc. Abstr.*, 1904 ; [II], **86**, 726.

Bousfield.—*J. Chem. Soc. Trans.*, 1915, **107**, 1781-97.

Heat of Formation.

Thomsen.—*Thermochem. Untersuch.*, **2**, 199.

$(NO_3)'$ Ion.

Kuhling.—*Z. angew. Chem.*, 1902, **15**, 1257-61 ; *J. Chem. Soc. Abstr.*, 1903 ; [II], **84**, 203.

P. Bogdan.—*Z. Elektrochem.*, 1907, **13**, 596-8 ; *J. Chem. Soc. Abstr.*, 1907 ; [II], **92**, 734.

F. Kohlrausch.—*Z. Elektrochem.*, 1907, **13**, 645-6 ; *J. Chem. Soc. Abstr.*, 1907 ; [II], **92**, 840.

E. C. C. Baly, K. A. Burke, and E. A. Marsden.—*J. Chem. Soc. Trans.*, 1909, **95**, 1103.

Thomas.—*J. Amer. Leather Chem. Assoc.*, 1920, **15**, 133 ; *J. Amer. Chem. Soc. Abstr.*, 1920, **14**, 1469.

Constitution.

W. H. Perkin (senior).—*J. Chem. Soc. Trans.*, 1889, **55**, 724.

Aston and Ramsay.—*Ibid.*, 1894, **65**, 169.

Veley and Manley.—*Phil. Trans.*, 1898, **191** A, 365.

Hartley.—*J. Chem. Soc. Trans.*, 1903, **83**, 658-66 ; *Roy. Soc. Proc.*, *Dublin*, 1905 ; [II], **10**, 373-7 ; *J. Chem. Soc. Abstr.*, 1905 ; [II], **88**, 815.

Veley.—*Chem. News*, 1911, **104**, 309.

Schaeffer and Niggemann.—*Z. anorg. Chem.*, 1916, **97**, 285-311 ; *J. Chem. Soc. Abstr.*, 1917 ; [II], **112**, 61.

Fuming Nitric Acid.

Lunge and Marchlewski.—*Z. angew. Chem.*, 1892, **10-12**, 330-1 ; *J. Chem. Soc. Abstr.*, 1893 ; [II], **64**, 66.

Marchlewski.—*Z. anorg. Chem.*, 1892, **1**, 368 ; **2**, 18.

Marchlewski and Liljernstein.—*Z. anorg. Chem.*, 1894, **5**, 288 ; *J. Chem. Soc. Abstr.*, 1894 ; [II], **66**, 41.

Vanino.—*Ber.*, 1899, **32**, 1392-3 ; *J. Chem. Soc. Abstr.*, 1899 ; [II], **76**, 479.

Bousfield.—*J. Chem. Soc. Trans.*, 1919, **115**, 45.

Chemical Properties.

DECOMPOSITION BY HEAT.

BERTHELOT.—*Comptes rend.*, 1898, **127**, 83-8 ; *J. Chem. Soc. Abstr.*, 1899 ; [II], **76**, 21.
CARIUS.—*Ber.* [IV], 828-34.

DECOMPOSITION BY LIGHT.

BERTHELOT.—*Comptes rend.*, 1898, **127**, 143-60 ; *J. Chem. Soc. Abstr.*, 1899 ; [II], **76**, 1.
VELEY AND MANLEY.—*Phil. Trans.*, 1908, **191** A, 367.
W. C. REYNOLDS AND W. H. TAYLOR.—*Chem. News*, 1911, **104**, 315.

DECOMPOSITION BY HYDROGEN.

FARADAY.—*Phil. Trans.*, 1834.
BOURGOIN.—*J. Pharm. Chim.*, 1871 ; [IV], **13**, 266-70 ; *J. Chem. Soc. Abstr.*, 1871, **9**, 885.
J. H. GLADSTONE AND A. TRIBE.—*J. Chem. Soc. Trans.*, 1879, **35**, 172.
LUCKNOW.—*Z. anal. Chem.*, 1880, **19**, 11.
D. TOMMASI.—*J. Phys. Chem.*, 1898, **2**, 229 ; *J. Chem. Soc. Abstr.*, 1899 ; [II], **76**, 138.
BERTHELOT.—*Comptes rend.*, 1898 ; [I], **127**, 27-9 ; *J. Chem. Soc. Abstr.*, 1899 ; [II], **76**, 21.
J. W. WILKINSON.—*Amer. Electrochem. Soc.*, April to May 1898.
FREER AND HIGLEY.—*Amer. Chem. J.*, 1899, **21**, 377-92.
OSTWALD.—*Grundliss d'allgem. Chem.*, 1899, p. 440.
J. TAFEL.—*Z. anorg. Chem.*, 1902, **31**, 289-325 ; *J. Chem. Soc. Abstr.*, 1902 ; [II], **82**, 559.
W. H. EASTON.—*J. Amer. Chem. Soc.*, 1903, **25**, 1042-4 ; *J. Soc. Chem. Ind.*, 1903, **22**, 1258.
J. W. TURRENTINE.—*J. Phys. Chem.*, 1906, **10**, 715-20 ; *J. Chem. Soc. Abstr.*, 1907 ; [II], **92**, 81.
H. E. PATTEN.—*Trans. Amer. Electrochem. Soc.*, 1907, **12**, 325-98 ; *J. Soc. Chem. Ind.*, 1908, **27**, 575.
J. W. WILKINSON.—*Electrochem. Ind.*, 1908, **6**, 229 ; *J. Soc. Chem. Ind.*, 1908, **27**, 756.
H. E. PATTEN AND W. J. M'CAUGHEY.—*Amer. Electrochem. Soc.*, May 1910 ; *Met. and Chem. Eng.*, 1910, **8**, 348 ; *J. Soc. Chem. Ind.*, 1910, **29**, 813.
W. C. REYNOLDS AND W. H. TAYLOR.—*J. Soc. Chem. Proc.*, 1911, **27**, 306, *ibid.*, *Trans.*, 1912, **101**, 131.
BANERJEE AND BANERJEE.—*J. Chem. Soc. Proc.*, 1911, **27**, 326.
KLEMENC.—*Z. Elektrochem.*, 1921, **27**, 110-12 ; *J. Chem. Soc. Abstr.*, 1921 ; [II], **120**, 297.
BURDICK.—*J. Amer. Chem. Soc.*, 1921, **43**, 518-30 ; *J. Chem. Soc. Abstr.*, 1921 ; [II], **120**, 313.
BROWN.—*J. Phys. Chem.*, 1921, **25**, 429-54.

ACTION ON METALS.

General.

Thénard.—*Traité de Chimie*, 1834, p. 363.
Gmelin.—*Chemistry Eng. Trans.*, 1849, **2**, 397.
Regnault.—*Cours Elémentaire de Chimie*, 1851, **1**, 142.
Pelouze and Fremy.—*Traité de Chimie*, 1860, **1**, 351.
Mendelejeff.—*Third Eng. Edition*, **1**, 297-8.
Miller.—*Chemistry*, 1874, **2**, 154.
Acworth and Armstrong.—*J. Chem. Soc. Trans.*, 1877, **15**, 54.

Cu, Zn, Hg, Ag.

Acworth.—*J. Chem. Soc.*, 1875, **13**, 828.
Divers.—*J. Chem. Soc. Trans.*, 1883, **43**, 443-66.
Veley.—*J. Soc. Chem. Ind.*, 1891, **10**, 204-10; *Phil. Trans.*, 1891, **182 A**, 279-339; *Roy. Soc. Proc.*, **48**, 458-9; *J. Chem. Soc. Abstr.*, 1891, **60**, 525.
Montemartini.—*Atti. R. Accad. Lincei*, 1892; [V], **1**, 63.
Freer and Higley.—*Amer. Chem. J.*, 1899, **21**, 377-92; *J. Chem. Soc. Abstr.*, 1899; [II], **76**, 480.
Gladstone.—*Phil. Mag.*, 1900; [V], **50**, 231.
Divers.—*J. Soc. Chem. Ind.*, 1904, **23**, 1182-5.

Cu, Zn, Mg.

Ewart.—*Pharm. J.*, 1902; [1649], **68**, 82; *Nature*, **65**, 128.
A. van Bijlert.—*Z. physik. Chem.*, 1899, **31**, 103-13; *J. Chem. Soc. Abstr.*, 1900; [II], **78**, 204.

Cu, As, Sb, Bi.

J. H. Stansbie.—*J. Soc. Chem. Ind.*, 1906, **25**, 1071-6.

Cu, Bi, Ag, As.

J. H. Stansbie.—*J. Soc. Chem. Ind.*, 1908, **27**, 365-7.

Cu, Ag, Pb, Cu, Alloys.

J. H. Stansbie.—*J. Soc. Chem. Ind.*, 1909, **28**, 268-74; *J. Soc. Chem. Ind.*, 1913, **32**, 311-19; *ibid.*, pp. 1135-6.

Copper.

Millon.—*Comptes rend.*, 1842, **14**, 904.
Veley.—*J. Soc. Chem. Ind.*, 1889, **8**, 858.
Freer and Higley.—*Amer. Chem. J.*, 1893, **15**, 71-81; *J. Chem. Soc. Abstr.*, 1893; [II], **64**, 272.
J. H. Stansbie.—*J. Soc. Chem. Ind.*, 1906, **25**, 45-50.
E. H. Rennie, A. J. Higgin, and W. T. Cooke.—*J. Chem. Soc. Proc.*, 1908, **24**, 141; *ibid.*, *Trans.*, 1908, **93**, 1162.
Drapier.—*Comptes rend.*, 1914, **158**, 338-40.
N. R. Dhar.—*Proc. Acad. Sci. Amsterdam*, 1920, **22**, 570-5; *J. Amer. Chem. Soc. Abstr.*, 1920, **14**, 2286.
Bagster.—*J. Chem. Soc. Trans.*, 1921, **119**, 82-7.

Silver.

Russell.—*J. Chem. Soc.*, 1874, **12**, 3.
Divers.—*J. Chem. Soc.*, 1885, **47**, 231.
G. O. Higley and W. E. Davis.—*Amer. Chem. J.*, 1896, **18**, 587-90 ; *J. Chem. Soc. Abstr.*, 1896 ; [II], **70**, 560.

Aluminium.

A. Ditte.—*Comptes rend.*, **110**, 782-4.
Le Roy.—*Bull. Soc. Ind. Rouen*, 1891, **19**, 232 ; *J. Soc. Chem. Ind.*, 1892, **11**, 166.
Stillman.—*J. Amer. Chem. Soc.*, 1897, **19**, 711-16.
A. Trillat.—*Bull. Soc. d'Encour.*, 1915, **132**, 547-54 ; *J. Soc. Chem. Ind.*, 1915, **34**, 874.
R. Seligman and P. Williams.—*J. Soc. Chem. Ind.*, 1916, **35**, 665-71.
E. R. Hodges.—*Chem. News*, 1919, **119**, 64 ; *J. Chem. Soc. Abstr.*, 1919 ; [II], **116**, 414.
Anon.—*Chem. and Met. Eng.*, 1920, **22**, 230-1 ; *J. Amer. Chem. Soc. Abstr.*, 1920, **14**, 870.

Zinc.

Deville.—*Comptes rend.*, 1870, **70**, 20 and 550.
Montemartini and Colonna.—*Atti R. Accad. Sci. Torino*, 1907, **42**, 551-64.
Divers.—*J. Chem. Soc. Trans.*, 1883, **43**, 443-66.

Tin.

C. H. H. Walker.—*Proc. Chem. Soc.*, 1893, 114-5 ; *J. Soc. Chem. Ind.*, 1893, **12**, 449.
R. Engel.—*Comptes rend.* ; [XIX], **125**, 709-11 ; *J. Soc. Chem. Ind.*, 1898, **17**, 44.
van Leent.—*Rec. trav. chim. Pays. Bas.*, 1898, **17**, 86 ; *J. Soc. Chem. Ind.*, 1898, **17**, 767.
Kleinschmidt.—*Monatsh.*, 1918, **39**, 149-78 ; *J. Amer. Chem. Soc. Abstr.*, 1919, **13**, 2490.
Divers.—*J. Chem. Soc. Trans.*, 1883, **43**, 443-66.

Iron.

F. W. Richardson.—*J. Soc. Chem. Ind.*, 1917, **36**, 15.
Freer and Higley.—*Amer. Chem. J.*, 1899, **21**, 377-92 ; *J. Chem. Soc. Abstr.*, 1899 ; [II], **76**, 480.
Brown.—*J. Phys. Chem.*, 1921, **25**, 429-54.

Lead.

V. H. Veley.—*J. Soc. Chem. Ind.*, 1891, **10**, 206-10.
Lunge.—*Eng. and Min. J.*, 1893, pp. 8-10, 32, 56-7 ; *J. Soc. Chem. Ind.*, 1893, **12**, 146.

Pb and Cu.

FREER AND HIGLEY.—*Amer. Chem. J.*, 1899, **21**, 377-92; *J. Chem. Soc. Abstr.*, 1899; [II], **76**, 480.

HIGLEY.—*Amer. Chem. J.*, 1895, **17**, 18-27; *J. Chem. Soc. Abstr.*, 1895; [II], **68**, 164.

Mercury.

P. C. RÂY.—*J. Chem. Soc. Trans.*, 1911, **99**, 1012.

Platinum.

G. P. BAXTER AND F. L. GROVER.—*J. Amer. Chem. Soc.*, 1914, **36**, 1089-91; *J. Chem. Soc. Abstr.*, 1914; [II], **106**, 570.

"Passive" State.

HEATHCOTE.—*J. Soc. Chem. Ind.*, 1907, **26**, 899.

DUNSTAN AND HILL.—*J. Chem. Soc. Trans.*, 1911, **99**, 1853.

General Discussion.

SCHULZE.—*Trans. Faraday Soc.*, 1914, **9**, 266-73.

YOUNG AND HOGG.—*J. Phys. Chem.*, 1915, **19**, 617-49.

BENNETT AND BURNHAM.—*J. Phys. Chem.*, 1917, **21**, 107-49.

BROWN.—*J. Phys. Chem.*, 1921, **25**, 429-54.

ACTION ON NON-METALS.

WATSON.—*J. Soc. Chem. Ind.*, 1892, **11**, 226.

MONTEMARTINI.—*Gazz. Chim. Ital.*, 1898; [I], **28**, 397.

ACTION ON CELLULOSE.

CROSS AND BEVAN.—*Chem. News*, 1889, **60**, 13-14.

KNECHT.—*J. Soc. Dyers and Col.*, 1896, **12**, 89-90; *J. Soc. Chem. Ind.*, 1896, **15**, 449.

KNECHT AND LIPSCHITZ.—*J. Soc. Chem. Ind.*, 1914, **33**, 116-23.

REDUCTION BY NITRIC OXIDE.

VELEY.—*Roy. Soc. Proc.*, **52**, 27-54; *J. Chem. Soc. Abstr.*, 1893; [II], **64**, 413.

SAPOSCHNIKOFF.—*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 506-16; *J. Chem. Soc. Abstr.*, 1902; [II], **82**, 16; *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 375-81; *J. Chem. Soc. Abstr.*, 1900; [II], **78**, 722.

G. N. LEWIS AND A. EDGAR.—*J. Amer. Chem. Soc.*, 1911, **33**, 292-9; *J. Chem. Soc. Abstr*, 1911; [II], **100**, 264.

ACTION ON CAUSTIC SODA AT LOW TEMPERATURES.

PICTET.—*J. Soc. Arts.*, 1911, **59**, 678.

CHAPTER VII

INDUSTRIALLY IMPORTANT NITRATES

NITRATES AS A CLASS.

THE salts produced by the interaction of bases with nitric acid are known as nitrates, the general reaction being represented by the equation—

$$\underset{\text{Lime}}{CaO} + \underset{\text{Nitric acid}}{2HNO_3} = \underset{\text{Calcium nitrate}}{Ca(NO_3)_2} + \underset{\text{Water}}{H_2O}$$

Nitrates as a class are among the most important of all salts, as they are utilised to an enormous extent as fertilisers in soil cultivation to provide the supplies of nitrogen necessary for plant growth.

General Properties.

All normal nitrates are soluble in water, and this property distinguishes the salts of nitric acid from those of sulphuric and hydrochloric acid, some of which are insoluble in water. Certain nitrates (*e.g.*, mercuric and bismuth nitrates) are, however, readily hydrolysed by water with production of insoluble basic salts.

$$e.g.\quad \underset{\text{Normal salt}}{Bi(NO_3)_3} + 2H_2O = \underset{\text{Basic salt}}{Bi(OH)_2NO_3} + 2HNO_3$$

All nitrates are decomposed when heated with concentrated sulphuric acid with liberation of nitric acid.

$$e.g.\quad KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

All nitrates are decomposed on heating with liberation of oxygen, and thus they act like nitric acid as oxidising agents.

The alkali metal nitrates, on heating at a red heat, give nitrites and oxygen.

$$e.g.\quad 2KNO_3 = 2KNO_2 + O_2.$$

Stronger heating, however, leads to the evolution of oxygen, brown fumes, and a residue of the alkali metal oxides remains.

$$e.g. \quad 8KNO_3 = 8NO_2 + O_2 + 2K_2O + 2K_2O_2.$$

Silver nitrate also shows nitrite formation when heated just above its fusing point.

Ammonium nitrate behaves exceptionally on heating, being decomposed into nitrous oxide and steam.

$$NH_4(NO_3) = N_2O + 2H_2O.$$

Other nitrates do not show the intermediate nitrite decomposition stage, being decomposed direct into nitrogen oxides, oxygen, and metallic oxide.

$$e.g. \quad 2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

The large usage of nitrates in the manufacture of explosives is dependent on their capability of liberating oxygen readily when heated.

General Methods of Preparation.

1. Solution of metal in nitric acid—

$$e.g. \quad 2Ag + 4HNO_3 = \underline{2AgNO_3} + 2NO_2 + 2H_2O.$$

2. Reaction of oxide or hydroxide with nitric acid—

$$e.g. \quad (a) \quad Fe_2O_3 + 6HNO_3 = \underline{2Fe(NO_3)_3} + 3H_2O.$$

$$(b) \quad NH_4OH + HNO_3 = \underline{NH_4NO_3}.$$

3. Reaction of carbonate or sulphide with nitric acid—

$$e.g. \quad (a) \quad CaCO_3 + 2HNO_3 = \underline{Ca(NO_3)_2} + CO_2 + H_2O.$$

$$(b) \quad BaS + 2HNO_3 = \underline{Ba(NO_3)_2} + H_2S.$$

4. Double decomposition of salts in solution—

$$e.g. \quad Ba(NO_3)_2 + CuSO_4 = \underline{Cu(NO_3)_2} + BaSO_4.$$

SODIUM NITRATE, $NaNO_3$ ("CHILI SALTPETRE"; "CUBIC NITRE").

Production.

The commercial production of sodium nitrate has been dealt with in Chapter I., pp. 1-37, under the heading of "Raw Materials for Nitric Acid Manufacture."

Pure Sodium Nitrate.

Production. — Chili nitrate is not a convenient source of the pure salt although it may be, and is, purified by repeated fractional crystallisation. One or other of the general methods of preparation (p. 361) serves to provide the pure material required only in small quantities for chemical laboratory practice.

Sodium Nitrate, $NaNO_3$.

Physical Characteristics.

Molecular Weight	85·01	Melting-point	313°
Specific Gravity	2.27 at 20°	Crystalline Form	Rhombohedral

Sodium Nitrate, $NaNO_3$.

Solubility in Water.[1]

	Grams $NaNO_3$ per 100 Grams.			Grams $NaNO_3$ per 100 Grams.	
t°	Solution.	Water.	t°	Solution.	Water.
0	42·2	72·9 to 73·0	80	59·7	148·0 to 148·0
10	44·7	80·8 ,, 80·5	100	64·3	180·0 ,, 175·8
20	46·7	87·5 ,, 88·0	120	68·6	218·0 ,, 208·8
25	47·6	91·0 ,, 92·0	180	78·1	356·7
30	48·7	94·9 ,, 96·2	220	83·5	506·0
40	50·5	102·0 ,, 104·9	225	91·5	1076·0
50	52·8	112·0 ,, 114·0	313	100·0	...
60	54·9	122·0 ,, 124·0			

Note.—Solubility data in this chapter are from Seidell's *Solubilities of Inorganic and Organic Substances*, 2nd edit., 1920.

Uses.

1. As a fertiliser.
2. In the manufacture of sulphuric acid.
3. For the manufacture of nitric acid.
4. For the manufacture of potassium and other nitrates.
5. In the manufacture of low grade gunpowder and certain other explosives.

POTASSIUM NITRATE, KNO_3 (SALTPETRE).

Sources.

1. In caliche (to the extent of an average of about 2 per cent.) along with sodium nitrate and other salts.

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[1] Mulder; Berkeley, 1904; see also Ditte, 1875; Maumee, 1864; Etard, 1894.

2. In surface accumulations on the soil in certain parts of India.

3. By interaction of potassium chloride and sodium nitrate in aqueous solution.

4. From so-called " Nitre Plantations."

Production.

From Chili Saltpetre.—The extraction of potassium nitrate as such from the caliche of Chili is not yet carried on to any considerable extent, though during the war some companies paid attention to the problem and separated considerable quantities of potassium nitrate, which normally would have been included in the ordinarily recovered nitrate of soda.

The separation of sodium and potassium nitrates when present in solution together depends on the greater solubility of sodium nitrate at low temperatures.

At 20° C.,	100 parts of water	dissolve	87.5 pt. $NaNO_3$	and	31.2 KNO_3.
,, 0° C.,	,,	,,	72.9	,,	13.3 ,,
,, − 15° C.,	,,	,,	60.0	,,	3.3 ,,

Patents relating to methods of separating potassium nitrate from sodium nitrate were taken out over twenty years ago, but to-day the bulk of the potassium nitrate present in the raw ores of Chili serves only as a potential source of contribution to the world's supplies of that salt.

During the normal crystallisation process for sodium nitrate in Chili, the mother liquor from the crystallising pans is saturated at air temperature with potassium nitrate in a solution of many other salts. Some potassium nitrate is deposited in the crystallising tanks owing to surface evaporation during the cooling process, and is a usual impurity (to the extent of 1 to 10 per cent.) in the commercial sodium nitrate.

By transferring the liquor in the crystallising pans to other pans when the temperature has become lowered to that corresponding to the saturation point of the solution in regard to potassium nitrate, a further crop of crystals containing about 20 per cent. of potassium nitrate is obtained.

HIGH POTASH NITRATE.—This is known as high potash (H.P.) nitrate.

Similar H.P. nitrate is obtained by artificial evaporation of the mother liquors from the crystallising pans. The sodium chloride content is largely deposited in the evaporators, being less soluble in the hot than in the cold solution The mixed crystals obtained on crystallising the hot liquors contain 93 to 95 per cent. total nitrates with a 25 to 30 per cent. KNO_3 content. In this process boric acid up to 3 per cent. exists as impurity, and there is a tendency for high sulphate and high magnesium contents.

By a process of refrigeration to −10° C. introduced in 1918 at Officina Delaware a much purer product is obtained. As already indicated, the solubility of potassium nitrate decreases much more rapidly than the solubility of sodium nitrate, when a solution of both salts is cooled. Further, at low temperatures there is no deposition of boric acid, magnesium salts, or chloride, though sulphates begin to deposit at −5° C.

Typical analyses of nitrates by both processes are as follows[1]:—

	H.P. Nitrate.	
	By the Evaporation Process.	By the Refrigeration Process.
Moisture	3·72 per cent.	0·79 per cent.
Insoluble	0·10 ,,	0·09 ,,
$NaCl$	0·76 ,,	0·56 ,,
Na_2SO_4	0·44 ,,	0·35 ,,
Nitrate (by difference)	94·98 ,,	98·21 ,,
CaO	0·16 ,,	0·04 ,,
MgO	0·44 ,,	0·20 ,,
$KClO_4$	0·55 ,,	0·30 ,,
H_3BO_3	3·00 ,,	0·17 ,,
KNO_3	28·07 ,,	42·00 ,,

By the addition of a small quantity of water to the mother liquor before refrigeration, a potassium nitrate content of 60 to 85 per cent. KNO_3 may be obtained. Crystals of this type on washing in centrifugals with carefully regulated quantities of pure water finally analyse 94·5 per cent. KNO_3.

As under the best conditions only 30 to 60 per cent. of the potassium content of the caliche is recovered as nitrate, there is plenty of opportunity for improvements in the processes now employed.

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[1] Holstein, *J. Ind. Eng. Chem.*, 1920, **12**, 290-93.

In India.—Potassium nitrate has been produced in India from very early times. For long the trade was a monopoly of the East India Company, who were under an obligation to supply the British Government before other consumers. The trade has always been subject to extreme fluctuations, the trend of political events having a direct effect on it. It attained its highest values from 1860 to 1864, at the time of the American Civil War, for at that period saltpetre was an essential constituent of explosives, and India had practically a monopoly of supplies. The average annual exports then amounted to over 30,000 tons, but the development of the South American nitrate industry caused the Indian trade gradually to decline, and exports had fallen to 13,000 or 14,000 tons per annum in the years immediately preceding the war. The war period witnessed the usual stimulation of the trade.

The most important centre of production is the Bihar section of the Gangetic plain. Here, an agricultural population of over 500 per square mile supplies an abundance of organic nitrogen, the climatic conditions are ideal for the growth of the so-called "nitrifying bacteria," the soil around the villages is well-stocked with potash from the universal use of wood and cow dung for fuel, and the continuous surface desiccation following a small rainfall, causes the subsoil water to bring to the surface an efflorescence of salts in which potassium nitrate is conspicuous. Saltpetre is also extracted in the United Provinces and in the Punjab.[1]

FACTORS IN FORMATION.—According to C. M. Hutchinson,[2] the factors determining the formation of potassium nitrate as a soil constituent are as follows:—

1. *Nitrifiable organic matter* in suitable proportion in the soil.
2. *Lime.*
3. *Water*, not only in sufficient amount for nitrification, but also distributed in the soil in such a way as not to interfere with aeration, and to provide the continual capillary rise to the surface.

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[1] Records of the Geological Survey of India. Annual Statement of the Seaborne Trade of British India. Accounts relating to the Seaborne Trade and Navigation of British India.

[2] Bulletin No. 68 of the Agricultural Research Branch, Pusa; *Nature*, 1917, **99**, 447.

FIG. 129.

FIG. 130.

[Face page 364.

4. *Climate*, ensuring a provision of adequate moisture and temperature during part of the year and complete, or nearly complete, absence of rainfall, coupled with low humidity during a sufficiently long period to ensure the capillary rise of subsoil water consequent on rapid surface evaporation.

The supply of saltpetre is almost entirely obtained from the soil in the immediate neighbourhood of human habitations, or of abandoned village sites, where nitrogenous organic refuse, consisting largely of excrementitious matter of men and cattle, has accumulated.

Crude Nitrate.—The surface soil, scraped to the depth of a quarter of an inch, is mixed with an equal quantity of residual earth from previous extractions, and put into a circular filter-bed, consisting of a mud wall and floor plastered with clay, and having a bottom layer of bamboos and straw. The earth is trodden down in this filter-bed and then water is poured over it. After percolating through the filter-bed the liquid is caught in an earthenware vessel. The first runnings contain most of the nitrate, mixed with common salt. The solution is concentrated in an open pan over a fire of wood or dead bamboo leaves, the ashes of which, being rich in potash, are added to the extracted earth, which is mixed afterwards with freshly gathered soil. The crude salt obtained on crystallising the concentrated liquor is sold, usually through a middleman, to the refiner, who works under Government supervision.[1]

The manufacture is controlled under licenses issued by the Northern India Salt Revenue Department, and the first portion of the work is done by a special caste which carries on the operations as an hereditary profession.

The crude nitrate earths contain on an average about 3 per cent. to 5 per cent. of saltpetre. The crude product of the Bihar and United Provinces yields 40 to 50 per cent. refined saltpetre, the Punjab crude about 30 per cent.[2]

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[1] Hutchinson, *Nature*, 1917, **99**, 447-48.

[2] The Mineral Industry of the British Empire and Foreign Countries —War Period — Nitrates, Imperial Mineral Resources Bureau, H.M. Stationery Office, 1920.

The following analyses of crude nitre, due to Hooper, and taken from Marshall's *Explosives*, 1915, are said to be typical:—

Crude Saltpetre.

	Farukhabad.		Okara.		Mozafferpore.	Burhanpura.
	I.	III.	I.	III.		
Potassium nitrate .	66·07	44·92	53·00	26·86	49·36	68·40
Calcium ,, .	...	...	2·60	...	3·28	2·60
Magnesium ,, .	2·54	4·80	...	12·24	7·44	2·12
Sodium chloride .	21·84	35·38	34·22	34·80	16·82	17·98
Sodium sulphate .	3·65	10·00	3·88	11·20	14·60	3·40
Insoluble . .	0·90	1·20	1·10	1·40	1·50	1·70
Water . . .	5·00	3·70	5·20	13·50	7·00	3·80
	100·00	100·00	100·00	100·00	100·00	100·00

REFINED NITRATE.—At the refineries the crude saltpetre is dissolved in boiling mother liquors from previous operations, the water content being such that most of the common salt and other impurities remain undissolved, while the potassium nitrate forms a saturated solution (*cf.* table of solubilities on p. 367). After settling, the hot liquor is run into wooden vats where it is allowed to crystallise.

The refined saltpetre is in the form of large brown crystals, and is sometimes further improved in quality by a process of washing with cold water. The following analyses, given by Leather and Mukerji, and taken from Marshall's *Explosives*, show the effect of this washing:—

Refined Saltpetre.

	Burhanpura.		Savan.		Bakramau.	
	Unwashed.	Washed.	Unwashed.	Washed.	Unwashed.	Washed.
Potassium nitrate .	90·70	94·91	81·98	91·55	88·63	94·70
Potassium sulphate .	...	...	5·44	0·93	0·15	0·15
Sodium sulphate .	0·91	0·03	...	...	...	...
Potassium chloride .	...	...	2·59	2·51	6·06	2·67
Sodium chloride .	5·40	3·12	7·05	1·68	0·07	0·10
Sand . . .	0·30	0·20	0·20	0·35	...	...

This refined or "grough" saltpetre requires further purification before it can be used for the manufacture of gunpowder and other explosives. The purification process is one of recrystallising and washing, the chief impurity (common salt) being reduced to less than 0·005 per cent.

Production of Saltpetre in India.

Year.	Quantity (long tons).	Value £.
1913	14,462	200,803
1914	15,489	272,462
1915	18,098	373,891
1916	25,056	607,488
1917	21,284	527,666
1918	24,741	589,190

The "Conversion" Process.—The process whereby potassium nitrate is produced by the interaction of potassium chloride and sodium nitrate in aqueous solution is known as the "Conversion Process," and is represented by the equation,

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

In dilute solution, all four salts would be present together, but advantage is taken in practice of the relative insolubility of sodium chloride in hot solutions compared with the other salts. By working with a limited supply of water, which is insufficient to retain the whole of the sodium chloride in solution, precipitation of this salt is effected, with practically complete conversion of the potassium chloride and sodium nitrate. The problem then becomes the separation of potassium nitrate and sodium chloride which are in hot saturated solution together.

The relative solubilities of potassium nitrate and sodium chloride in a solution saturated with both salts is shown in the following table, figures for which are taken from Seidell's *Solubilities of Inorganic Substances*, 1920:—

Temperature in °C.	Grams per 100 grams Water	
	KNO_3.	NaCl.
20	37·3	37·73
30	49·24	38·72
40	64·77	38·79
91	218·8	39·08

The conversion process was developed largely as a result of the large demand for potassium nitrate during the Crimean War. It became possible on a very large scale as a result of the discovery of cheap supplies of potassium chloride in the double chloride of potassium and magnesium known as carnallite, one of the Stassfurt salts. Meyerhoffer[1] studied the conditions of equilibrium between the reciprocal pairs of salts: KCl, $NaNO_3$ and NaCl, KNO_3, and the practical details of the conversion were thoroughly worked out.

Procedure.—Stassfurt potassium chloride, containing not less than 80 per cent. KCl, and commercial Chili saltpetre are boiled together in correct proportions (a slight excess of sodium nitrate being used) with mother liquors from a previous operation containing insufficient water to retain in solution all the sodium chloride produced in the reaction. After half an hour's boiling the liquor is filtered hot. The sodium chloride retained in the filters forms a by-product of the operation, and is suitably washed free from nitrate (it retains about 0·8 per cent. nitrate) and then dried. The hot filtrate, saturated with potassium nitrate and sodium chloride,[2] is run into cooling pans, where it is agitated during crystallisation. The mother liquor from the crystallising pans is used over again in a subsequent conversion. Such a liquor resulting after treatment of 5000 tons of Chili nitrate had the composition shown by the following table taken from Thorpe's *Dictionary of Applied Chemistry* :—

Potassium nitrate	26·4	per cent.
Sodium chloride	17·18	,,
,, sulphate	1·81	,,
Magnesium chloride	8·19	,,
Sodium nitrate	7·19	,,
,, iodide	0·76	,,

The saltpetre from the crystallising pans, containing 7 to 9 per cent. of sodium chloride and 0·5 to 0·7 per cent. of

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[1] *Ber.*, 1904, **37**, 261 *et seq.*

[2] According to Reinders (*Chem. Zeit. Rep.*, 1916, **40**, 305 ; *J. Soc. Chem. Ind.*, 1916, **35**, 1058) the addition of water to the saturated solution of potassium nitrate and sodium chloride prevents the separation of the latter salt and saves subsequent washing.

magnesium chloride, is drained, and then washed with refined saltpetre washings until the chloride content is down to below 2 per cent. It is then recrystallised from refined saltpetre washwaters, and the resulting product contains only 0·25 to 0·75 per cent. of sodium chloride. This saltpetre is now washed with pure water and the refined saltpetre resulting is drained and dried. The refined material contains less than 0·005 per cent. of sodium chloride.

The various washwaters used in the process, including liquors obtained in washing nitrate of soda bags, are evaporated as necessary and added to the mother liquors from the crystallising pans ready for incorporation with subsequent charges of raw materials. There is thus practically no loss.

Nitre Plantations.—"Nitre plantations" now only serve to provide small local supplies of potassium nitrate, though previous to the introduction of sodium nitrate and the development of the conversion process, Governments "cultivated" nitre plantations for production of the potassium nitrate required for gunpowder manufacture.

When dung and other animal nitrogenous refuse are stacked loosely in contact with wood-ashes in the presence of air, though protected from the weather, conditions are suitable for the production of potassium nitrate. The heaps may be periodically drenched with urine over a period of a year or two, by the end of which time the potassium nitrate can be washed out and purified by recrystallisation.

Nitrifying bacteria bring about the oxidation of the ammonia, produced in the decay of the organic matter, to nitric acid, which, in contact with the potassium carbonate of the wood-ashes, yields potassium nitrate.

Nitre production in India, already referred to, is brought about by the same series of reactions.

Where lime ashes or old mortar are added to the decaying heaps, calcium nitrate is also produced and has to be converted during lixiviation by boiling with wood-ashes.

The following advertisement, which appeared in the German newspapers towards the beginning of the second year of the war, is interesting as indicating a revival of the Government "nitre plantations"[1]:—

> "The women of Germany are commanded to save their chamber lye, as it is very needful to the cause of the Fatherland in the manufacture of nitre, one of the ingredients of gunpowder. Wagons, barrels, and tanks will be sent to the residences daily to collect and remove the same. (Signed) VON HINDENBURG."

Potassium Nitrate, KNO_3.

Physical Characteristics.

Molecular weight . .	101·11	Crystalline form .	Orthorhombic below 129·5° Rhombohedral above 129·5°
Specific gravity .	2·087 at 15°		
Melting-point . .	. 336°, 342°		

Solubility in Water.[2]

AVERAGE CURVE.

t°	Grams KNO_3 per 100 Grams.	
	Water.	Solution.
0	13·3	11·7
10	20·9	17·3
20	31·6	24·0
25	37·3	27·2
30	45·8	31·4
40	63·9	39·0
50	85·5	44·0
60	110·0	52·0

AVERAGE CURVE.

t°	Grams KNO_3 per 100 Grams.	
	Water.	Solution.
70	138·0	58·0
80	169·0	62·8
90	202·0	66·9
100	246·0	71·1
110	300·0	75·0
120	394·0	79·8
125	493·0	83·1

1000 grams H_2O dissolve 384·48 grams KNO_3 at 25° (Armstrong and Eyre, 1910-11).

One litre saturated solution in water contains 2·8 mols. = 283·11 grams KNO_3 at 20° (Rosenheim and Weinheber, 1910-11).

Uses.

1. For manufacture of gunpowder and other explosives.
2. For manufacture of fireworks.
3. In the glass industry.
4. For pickling meat.

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[1] *J. Ind. Eng. Chem.*, 1919, **11**, 779.

[2] Mulder; Andrae, 1884; Gerardin, 1865; Etard, 1894; Ost, 1878; at 31·25°, Köhler, 1897; Euler, 1904; Tilden and Shenstone, 1884; Berkeley, 1904.

AMMONIUM NITRATE, NH_4NO_3.

The introduction of ammonium nitrate in the preparation of explosives some forty years ago led to the patenting of many processes for the manufacture of this salt, apart from the generally accepted one of neutralising nitric acid with a solution of ammonia in water. That interest in this matter was well kept up is seen by reference to patent literature since that time. It remained, however, for the intensive application of ammonium nitrate for explosives during the recent war to bring about the successful commercial development of processes previously suggested, but not generally worked owing to the delicacy of control necessary in the operations involved, to the limited demand for ammonium nitrate, to the simplicity of the generally accepted method of preparation, and to the availability of nitric acid and ammonia for purposes of neutralisation.

Now that the technical difficulties of manufacture of ammonium nitrate without the use of nitric acid have been largely overcome, it is quite likely that efforts will be made to find outlets for this salt, additional to the comparatively restricted requirements of the post-war explosives industry.

Agriculture may come to absorb large quantities for fertilising purposes when the non-deliquescent salt, which can now be provided, is better known.

Manufacture.

1. By neutralisation of ammonia and nitric acid

(*a*) In aqueous solution.

$$NH_4OH + HNO_3 = NH_4NO_3.$$

(*b*) By passing ammonia gas into concentrated nitric acid.

$$NH_3 + HNO_3 = NH_4NO_3.$$

Process (*a*) is most favoured and was developed largely in conjunction with the production of dilute nitric acid by synthetic processes. The neutralisation is effected by running the acid into ammonia liquor in closed iron tanks provided with agitating gear and cooling coils. The resulting liquor, left slightly alkaline, is filtered, evaporated in vacuum evaporators, and then crystallised with agitation in order to prepare fine crystals free from entrained mother liquor. The crystals are then dried in hydro-extractors.

Process (*b*) consists in passing ammonia gas into strong nitric acid in vessels closed except for vapour outlets. The heat of the reaction is utilised to effect sufficient evaporation, so that on completion of the neutralisation process the neutral ammonium nitrate solution is sufficiently concentrated for crystallisation. This process is subject to appreciable losses.

Very pure ammonium nitrate may be obtained direct by the above processes.

2. By the interaction of calcium nitrate with carbonate or sulphate of ammonia in aqueous solution.

$$(a)\ (NH_4)_2CO_3 + Ca(NO_3)_2 = 2NH_4NO_3 + CaCO_3.$$
$$(b)\ (NH_4)_2SO_4 + Ca(NO_3)_2 = 2NH_4NO_3 + CaSO_4.$$

These reactions are simple instances of double decomposition with precipitation of an insoluble salt which is readily removed by filtration. The initial purity of the ammonium nitrate produced is largely dependent on the quality of the calcium nitrate employed in the conversion.

3. By the interaction of ammonia, carbon dioxide and sodium nitrate solution.

$$NaNO_3 + NH_3 + H_2O + CO_2 = NH_4NO_3 + NaHCO_3.$$

This is a modification of the well-known ammonia soda process, and was first suggested by Gerlach in 1875. The technical difficulties due to reversibility of the reaction and accumulation of impurities in the mother liquor have now been largely overcome.

4. By the interaction of sodium nitrate and ammonium sulphate or chloride in aqueous solution.

$$(a)\ (NH_4)_2SO_4 + 2NaNO_3 = 2NH_4NO_3 + Na_2SO_4.$$
$$(b)\ NH_4Cl + NaNO_3 = NH_4NO_3 + NaCl.$$

The successful working of method No. 4 is covered by a number of patents, for details of which the reader is referred to patent literature and to pp. 401-16.

Some details of the manufacture as carried out at the U.S.A. Government plant at Perryville are given in two articles in the *Chemical and Metallurgical Engineering for* 1919,[1] and these articles have provided matter for the following account of the process.

The nitrate of soda used was refined on the plant from Chilian nitrate. Elimination of pyridene and other coal-tar bases and free sulphuric acid from the ammonium sulphate was effected by the addition of soda ash during the digestion of the ammonium sulphate and sodium nitrate. This soda-ash treatment also served to precipitate any alkaline earth salts present in the refined nitrate. The reaction was effected in a series of connected horizontal digesters where ammonium sulphate and sodium nitrate in the ratio of 41·9 : 59·3 were boiled with hot mother liquors from previous working, with thorough agitation by live steam. The reaction was completed when, on evaporating some of the liquor to dryness and subliming the ammonium salts, no sulphate was found in the sublimate. The hot saturated solution was filtered in rotary filters, diluted with water under carefully controlled conditions in order to prevent precipitation of sodium salts, cooled to about 38° C., and then run into crystallising pans in a room where the temperature and humidity of the air were controlled so as to avoid evaporation of the solution of definite relative concentrations, with a view to getting a yield of ammonium nitrate of known purity. When the concentration of ammonium nitrate in the liquor was sufficiently low, the liquor was drained away ready for evaporation and further use in the digesting process, and the ammonium nitrate crystals were dried in hydro-extractors.

The solubility curves in Fig. 131 indicate the respective solubilities of the reacting salts in 100 parts of water, each salt considered singly. Points (0, 0*b*, 0*c*) and (3, 3*b*, 3*c*) indicate the respective solubilities of ammonium nitrate, sodium nitrate, and sodium sulphate in 100 grams of water when present together, at the temperatures indicated, in saturated solution. Besides the three well-known anhydrous, hepta-, and deca-hydrate phases of sodium sulphate, and the five enantiotrophic crystalline phases of ammonium nitrate, the following four

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[1] Anon., *Chem. and Met. Eng.*, 1919, **20**, 320-6, and Bolling, pp. 401-5.

double salts exist to complicate matters and give impure yields:—

1. $Na_2SO_4 . NaNO_3 . H_2O$.
2. $Na_2SO_4 . (NH_4)_2SO_4 . 4H_2O$.
3. $(NH_4)_2SO_4 . 2NH_4NO_3$.
4. $(NH_4)_2SO_4 . 3NH_4NO_3$.

It is seen from Fig. 131 that if the saturated liquor at 97° C. were cooled direct to 20° C., the solution would be supersaturated with respect to the three salts present and a mixture of these salts would crystallise.

The process cycle shown in Fig. 131 gives broadly an indication of the method used at Perryville for effecting selective resolution of ammonium nitrate from the saturated solution obtained in the digestion. In cooling during the filtration process care was taken to keep the temperature above 64° C. to avoid precipitation of sodium salts. The addition of water at this point served to keep the sodium salts in solution during further cooling, and to decrease the concentration of ammonium nitrate to such an extent that cooling led to the crystallisation of the desired β rhombic modification. The resulting product contained 94 per cent. ammonium nitrate and 2 per cent. moisture.

Crystalline Forms.

Ammonium nitrate exists in five crystalline forms, the ranges of stability of which are marked by four well-defined transition temperatures. The following table, by Early and Lowry,[1] shows the crystalline form, change of state, and transition temperatures for these five crystalline forms known as α, β, γ, δ, and ϵ ammonium nitrates:—

Form of Salt.	Crystalline System.	Change of State.	Transition Temperature.
Liquid	...	ϵ to liquid	169·6°
ϵ	Cubic		
δ	Rhombohedral or tetragonal	δ to ϵ	125·2°
γ	Rhombic or monosymmetric	γ to δ	84·2°
β	Rhombic	β to γ	32·1°
α	Tetragonal	α to β	− 16, − 18°

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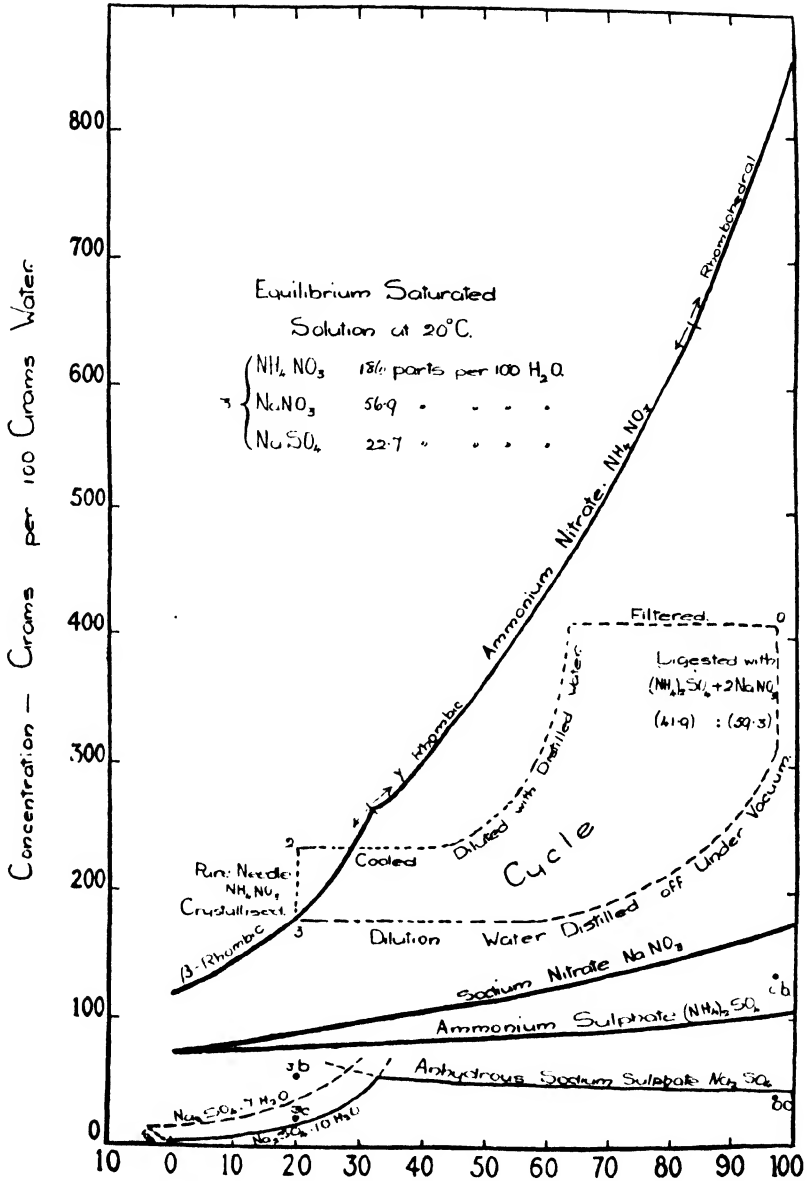
[1] *J. Chem. Soc. Trans.*, 1919, **115**, 1387.



Temperature in °C.

FIG. 131.

The β rhombic modification is obtained in fine needle-shaped crystals and is the form usually met with. It alone has the commercial advantage of not caking into hard masses on storing and can be conveniently handled.

The γ rhombic modification is a pseudomorph of the β, being formed when the latter is heated above 32°. If β crystals are heated beyond the β, γ transition point without stirring, the γ modification preserves the external characteristics of the β. If, however, the crystals are stirred during heating they break down into a very fine powder, which on storing in presence of moisture becomes cemented into a hard stone-like mass. On this account the γ form is not a suitable one for commercial purposes.

The change in form from β to γ is accompanied by an expansion of about 3 per cent., the relative densities of the two varieties being 1·725 and 1·66.

The latent heat of the change from γ to β is 5 calories per gram.

The transition at 84·2° is accompanied by a slight contraction in volume and an absorption of heat, the density becoming 1·69 and the latent heat being 5·3 calories per gram. This latent heat of transition at 84·2° is made use of in filling shells with a fused mixture of four parts NH_4NO_3 to one part T.N.T., the reserve of heat thus available serving to keep the mixture sufficiently fluid during filling.

The fourth solid phase, the δ modification, is one to be avoided in the production of ammonium nitrate for explosives since it sets to a glue-like mass.

The melting-point of ammonium nitrate, 169·6°, is very sensitive to the influence of traces of moisture.

Drying.

In an investigation of the caking, during drying, of ammonium and other nitrates, Lowry and Hemmings[1] came to the following conclusions:—(1) Caking is not caused directly by change of state, but this gives rise directly only to disintegration and to liberation of moisture from the partially dried crystals; the immediate cause of caking is the cementing

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 102-4.

effect on the tiny particles of the disintegrated salt of moisture released during the change of crystalline form.

(2) Liberation of enclosed moisture can also be effected by mechanical disintegration, and this may give rise to caking in precisely the same way as the disintegration and liberation of moisture consequent upon change of state, although the effects are much less pronounced. In the absence of moisture, mechanical disintegration would probably not give rise to caking.

(3) In an edge runner mill the moisture is able to evaporate as fast as it is released by milling, a fact that is frequently made use of as a convenient method of drying, *e.g.*, in the manufacture of gunpowder. Under these conditions the effect of the released moisture is only slight, and the mechanical working does not suffice to produce any serious caking of the salt.

Evaporation of Solutions.

Prideaux and Caven[1] come to the following conclusions regarding the tendency for ammonium nitrate to decompose during evaporation of its aqueous solutions:—

1. The hydrolysis of ammonium nitrate which occurs when an aqueous solution of this salt is evaporated in an acid-resisting vessel is very small and the loss is consequently inappreciable.
2. There is considerable loss of ammonia when ammonium nitrate solution is evaporated in contact with iron, accompanied by corrosion of the iron and consequent pollution of the residual salt. This is due to interaction between the iron and the hydrolytic nitric acid, with concomitant loss of ammonia.
3. The substitution of aluminium for iron as the material of the containing vessel almost entirely obviates loss of ammonia because of the inertness of this metal towards nitric acid.

Ammonium Nitrate, NH_4NO_3.

Physical Characteristics.

Molecular weight	80·05	Melting-point	169·6°
Specific gravity	1·72 at 15°	Crystalline form	Rhombic (see p. 374)

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1919, **38**, 353-55.

Solubility in Water.[1]

t°	Sp. Gr. Solution.	Grams NH_4NO_3 per 100 Grams.		Solid Phase.
		Solution.	Water.	
0	...	54·19	118·3	NH_4NO_3 rhomb. β.
12·2	1·2945	60·53	153·4	"
20·2	1·3116	65·80	192·4	"
25·0	1·3197	68·17	214·2	"
30·0	1·3299	70·73	241·8	"
32·1	1·3344	71·97	256·9	NH_4NO_3 rhomb. β + rhomb. α.
35·0	1·3394	72·64	265·8	NH_4NO_3 rhomb. α.
40·0	1·3464	74·82	297·0	"
50·0	...	77·49	344·0	"
60·0	...	80·81	421·0	"
70·0	...	83·32	499·0	"
80·0	...	85·25	580·0	"
90·0	...	88·08	740·0	NH_4NO_3 rhombohedral?
100·0	...	89·71	871·0	"

Uses.

1. For explosives.
2. For the manufacture of nitrous oxide.
3. For fireworks.
4. As a fertiliser.
5. For the production of low temperatures in laboratory practice. Equal parts of finely powdered ammonium nitrate and water mixed together cause a temperature lowering from +15° to −10°.

CALCIUM NITRATE, $Ca(NO_3)_2 \cdot 4H_2O$.

Calcium nitrate has assumed commercial importance as a result of its manufacture at Notodden in Norway as a means of fixing the synthetic nitric acid produced by the Birkeland-Eyde process.

Manufacture.

1. By neutralisation of dilute nitric acid with limestone.

At Notodden, dilute nitric acid of about 50 per cent. HNO_3 is neutralised by limestone in a series of granite tanks, with

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[1] Schwarz, Ostwald's *Lehrbuch*, 2nd edition, p. 425; Müller and Kaufmann, *Z. physik. Chem.*, 1901-1902, **42**, 497.

final addition of lime, and the neutral solution of ammonium nitrate is concentrated in vacuum evaporators either for the production of the crystalline tetrahydrate, or more generally for the production of a partially dehydrated material containing 13 per cent. of nitrogen. In the latter case, a proportion of lime is added just before the concentrated liquor is allowed to solidify in order to get a basic nitrate, $Ca(NO_3)_2$, $Ca(OH)_2$, which is not so hygroscopic. The product is utilised as a fertiliser under the name of "Norge saltpetre" or "Nitrate of Lime," its purity being dependent on the purity of the limestone used.

Platou[1] gives the following average composition of calcium nitrate as manufactured in the Pyrenees, by neutralising nitric acid with limestone:—

$Ca(NO_3)_2$	76·15 per cent.
$Ca(NO_2)_2$	0·05 "
CaO	0·15 "
MgO	0·30 "
$CaCO_3$	0·55 "
$MgCO_3$	0·35 "
Fe_2O_3	0·10 "
Al_2O_3	0·40 "
SiO_2	0·50 "
H_2O	21·45 "
	100·00

2. By double decomposition of sodium nitrate and calcium chloride in aqueous solution,

$$2NaNO_3 + CaCl_2 = Ca(NO_3)_2 + 2NaCl.$$

This method is only of local interest since it cannot compete commercially with method 1, which is able to produce sufficient calcium nitrate to meet present trade requirements.

During the war, the method was used on the large scale for the production of calcium nitrate to be used in the manufacture of ammonium nitrate.

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[1] *Chim. et Ind.*, 1920, **3**, 310-12; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, **39**, 401.

SUGGESTED METHODS.

(*a*) By dry absorption of nitrogen oxides in quicklime. When gases containing oxides of nitrogen, such as are obtained in the arc furnace, are passed over specially prepared quicklime at a temperature of 300 to 400° C., the nitrogen oxides are absorbed with production of calcium nitrate and calcium nitrite. By continuing the passage of the gases, however, the nitrite is converted into nitrate. This process, developed by Schloessing, has been tried upon a large experimental scale at Notodden, when a nitrate of 14·5 per cent. nitrogen was obtained and, it is said, generally satisfactory results were achieved.

Oswald[1] states that loss of nitrogen occurs in the interaction of lime and nitrogen peroxide as indicated in the following equation:—

$$4CaO + 10NO_2 = 4Ca(NO_3)_2 + N_2.$$

(*b*) An interesting but not yet commercial method for the production of calcium nitrate was outlined by Müntz and Lainé,[2] who showed the possibility, under prescribed conditions, of intensifying the oxidation effect of nitrifying bacteria on dilute solutions of ammonium salts in presence of peat. By using very dilute solutions of ammonium sulphate in presence of sufficient lime to combine with the nitric acid produced by oxidation, and circulating the solutions repeatedly over the peat, they were able to obtain solutions containing 22 per cent. of calcium nitrate equivalent to a production of 6·5 kg. calcium nitrate per cubic metre of peat in twenty-four hours.

It is interesting to compare this with the yield of an old "nitre plantation," which yielded about 5 kg. potassium nitrate per cubic metre in two years.

Calcium Nitrate, $Ca(NO_3)_2 . 4H_2O$.

Physical Characteristics.

Molecular weight	236·15	Melting-point	43°
Specific gravity	1·878 at 18°		(anhydrous) 561°
		Crystalline form	Monoclinic

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[1] *Annalen*, 1914, **61**, 32.

[2] *Comptes rend.*, 1905, **141**, 861-67 ; *ibid.*, 1906, **142**, 430-35 ; *J. Soc. Chem. Ind.*, 1905, **24**, 1301 ; *ibid.*, 1906, **25**, 275.

Solubility in Water.[1]

t°	Grams $Ca(NO_3)_2$ per 100 Grams Sat. Sol.	Solid Phase.	t°	Grams $Ca(NO_3)_2$ per 100 Grams Sat. Sol.	Solid Phase.
-0·4	1·4	Ice	40	66·21	$Ca(NO_3)_2 . 4H_2O$
-1·4	4·78	"	42·4	68·68	"
-1·9	6·53	"	42·4	68·74	"
-3·05	10	"	42·7	...†	"
-4·15	12·98	"	42·45	71·7	"
-15·7	33·13	"	40	70·37	$Ca(NO_3)_2 . 3H_2O$
-21·7	38·7	"	45	71·45	"
-28·7	...*	"	50	73·79	"
-26·7	43·37	$Ca(NO_3)_2 . 4H_2O$	51	74·73	"
-10	47·31	"	51·1	...†	"
0	50·50	"	49	77·49	$Ca(NO_3)_2 . 2H_2O$
5	51·97	"	51	78·05	"
10	53·55	"	55	78·16	$Ca(NO_3)_2$
15	54·94	"	80	78·2	"
20	56·39	"	100	78·43	"
25	57·98	"	125	78·57	"
30	60·41	"	147·5	78·8	"
35	62·88	"	151	79	"

* Eutectic. † Melting-point.

Solubility of the Unstable Calcium Nitrate Tetrahydrate β in Water.[2]

t°	Grams $Ca(NO_3)_2$ per 100 Grams Sat. Sol.	Solid Phase.
0	50·17	α $Ca(NO_3)_2 . 4H_2O$
22·2	56·88	"
25	57·90	"
30	60·16	"
30	61·57	β $Ca(NO_3)_2 . 4H_2O$
34	63·66	"
35	62·88	α $Ca(NO_3)_2 . 4H_2O$
38	64·34	"
38	66·65	β $Ca(NO_3)_2 . 4H_2O$
39	67·93	"
39·6 (m. pt.)	69·50	"
39 (reflex pt.)	75·34	"
40	66·22	α $Ca(NO_3)_2 . 4H_2O$
42·7 (m. pt.)	69·50	"
42·4 (reflex pt.)	71·70	"
25	77·30	$Ca(NO_3)_2$

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[1] Basset and Taylor, 1912.

[2] Results supplementary to the above (Taylor and Henderson, 1915).

Uses.

1. As a fertiliser.
2. For the preparation of other nitrates.
3. For the manufacture of nitric acid.

$$Ca(NO_3)_2 + H_2SO_4 = 2HNO_3 + CaSO_4.$$

4. For fireworks.

BARIUM NITRATE, $Ba(NO_3)_2$.

Manufacture.

1. By solution of the native carbonate, witherite, in nitric acid.

$$BaCO_3 + 2HNO_3 = Ba(NO_3)_2 + CO_2 + H_2O.$$

2. By solution of the sulphide, prepared by reduction of the native sulphate, barytes, in nitric acid.

$$BaS + 2HNO_3 = Ba(NO_3)_2 + H_2S.$$

3. By heating finely powdered barium carbonate or sulphide with calcium nitrate solution under pressure.

$$BaCO_3 + Ca(NO_3)_2 = Ba(NO_3)_2 + CaCO_3.$$

4. By double decomposition of sodium nitrate and barium chloride in aqueous solution.

$$2NaNO_3 + BaCl_2 = Ba(NO_3)_2 + NaCl.$$

Physical Characteristics.

Molecular weight .	261·39	Melting-point	595°
Specific gravity .	3·24 at 23°	Crystalline form .	Cubic (octahedral)

Solubility in Water.[1]

t°	Grams $Ba(NO_3)_2$ per 100 Grams.		t°	Grams $Ba(NO_3)_2$ per 100 Grams.	
	Water.	Solution.		Water.	Solution.
0	5·0	4·8	80	27·0	21·3
10	7·0	6·5	100	34·2	25·5
20	9·2	8·4	120	42·0	29·6
25	10·4	0·4	140	50·0	33·3
30	11·6	10·6	160	58·0	36·7
40	14·2	12·4	180	67·0	40·1
50	17·1	14·6	200	76·0	43·2
60	20·3	16·9	215	84·5	45·8

100 grams sat. aqueous solution contains 4·74 grams $Ba(NO_3)_2$ at 0° (Coppadoro, 1911).

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[1] Mulder; Gay Lussac; Etard, *Ann. Chim. Phys.*, 1894; [VII], **2**, 528; Euler, *Z. physik. Chem.*, 1904, **49**, 315.

Uses.

1. For fireworks. 2. For explosives.

STRONTIUM NITRATE, $Sr(NO_3)_2$.

Manufacture.

1. By solution of the native carbonate, strontianite, in nitric acid.

$$SrCO_3 + 2HNO_3 = Sr(NO_3)_2 + H_2O + CO_2.$$

2. By solution of strontium sulphide, obtained by reduction of the native sulphate, celestine, in nitric acid.

$$SrS + 2HNO_3 = Sr(NO_3)_2 + H_2S.$$

3. By heating finely powdered strontium carbonate or sulphide with calcium nitrate solution under pressure.

$$SrCO_3 + Ca(NO_3)_2 = Sr(NO_3)_2 + CaCO_3.$$

4. By double decomposition of sodium nitrate and strontium chloride in aqueous solution.

$$2NaNO_3 + SrCl_2 = Sr(NO_2)_2 + 2NaCl.$$

Strontium Nitrate $\begin{cases} Sr(NO_3)_2 \text{ from warm solutions.} \\ Sr(NO_3)_2 + 4H_2O \text{ from cold solutions.} \end{cases}$

Physical Characteristics, $Sr(NO_3)_2$.

Molecular weight	. 211·65	Crystalline form	Cubic (octahedral). —(with $4H_2O$) monoclinic.
Specific gravity	. 2·962 at 4°		
Melting-point	decomposes at 645°		

Solubility in Water.[1]

t°	d_4^t of Sat. Sol.	Grams $Sr(NO_3)_2$ per 100 Grams H_2O.	Solid Phase.
0·58	1·28561	40·124	$Sr(NO_3)_2 . 4H_2O$
14·71	1·39380	60·867	„
26·40	1·48831	82·052	„
29·06	1·51098	87·648	„
29·3	...	...	„ $+ Sr(NO_3)_2$
30·28	1·51441	88·577	$Sr(NO_3)_2$
32·58	1·51408	88·943	„
39·74	1·51282	90·086	„
47·73	1·51150	91·446	„
61·34	1·51048	93·856	„
68·96	1·51057	95·576	„
78·98	1·51091	97·865	„
88·94	1·51174	100·136	„

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[1] Berkeley and Appleby, 1911.

Uses.

1. For fireworks. 2. For explosives.

SILVER NITRATE, $AgNO_3$.

Preparation.

By dissolving silver in nitric acid.

$$2Ag + 4HNO_3 = 2AgNO_3 + 2NO_2 + 2H_2O.$$

It is obtained thus in the commercial separation of silver and gold by the "parting" process.

Copper nitrate is often present as impurity in the silver nitrate solution so obtained. The copper is removed by evaporating to dryness and igniting the mixed residues at a temperature sufficient to decompose the copper nitrate but not the silver nitrate. The latter may then be dissolved from its admixture with the insoluble copper oxide. Another way of purification is to precipitate the metals as hydroxides in a portion of the mixed nitrates solution, and add the precipitated hydroxides to the remaining solution. The silver hydroxide displaces copper as hydroxide which may then be filtered off.

The solution of silver nitrate is evaporated and allowed to crystallise.

Physical Characteristics.

Molecular weight .	169·89	Crystalline form	Rhombic below 159° Monoclinic above 159°
Specific gravity .	4·35 at 19°		
Melting-point . . .	218°*		

* Decomposes at a red heat.

Solubility in Water.[1]

t°	Grams $AgNO_3$ per 100 Grams.			t	Grams $AgNO_3$ per 100 Grams.		
	Solution.		Water.		Solution.		Water.
− 5	48 (Etard)	...	...	50	79 (Etard)	82	455
0	53	55	122	60	81·5	84	525
10	62	63	170	80	85·5	87	669
20	68	69	222	100	88·5	90·5	952
25	70·5	72	257	120	91	95	1900
30	72·5	75	300	140	93·5	...	...
40	76·5	79	376	160	95	...	...

100 grams sat. aq. solution contain 47·1 grams $AgNO_3$ at −7·3° (= Eutectic) (Middleberg, 1903).

100 grams sat. aq. solution contain 65·5 grams $AgNO_3$ at 15·5° (Greenish and Smith, 1903).

100 grams sat. aq. sol. contain 73 grams $AgNO_3$ at 30° (Schreinemakers and de Baat, 1910).

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[1] Etard, 1894; Kremers, 1854; Tilden and Shenstone, 1884.

Uses.

1. For photographic purposes.
2. As a chemical reagent.
3. As "lunar caustic" in pharmacy.
4. For preparation of marking inks.

LEAD NITRATE, $Pb(NO_3)_2$.

Preparation.

By dissolving lead or litharge in nitric acid.

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Physical Characteristics.

Molecular weight	331·2	Melting-point	decomposes
Specific gravity	4·53 at 20°	Crystalline form	cubic

Solubility in Water.[1]

t	Grams $Pb(NO_3)_2$ per 100 Grams.			t°	Grams $Pb(NO_3)_2$ per 100 Grams.		
	Water.		Solution.		Water.		Solution.
0	36·5	38·8	27·33	40	69·4	75	41·9
10	44·4	48·3	31·6	50	78·7	85	45
17	50	54	34·2	60	88	95	47·8
20	52·3	56·5	35·2	80	107·6	115	52·7
25	56·4	60·6	36·9	100	127	138·8	57·1
30	60·7	66	38·8	17	52·76*	...	34·54*

* Euler.

Density of saturated solution at 17 = 1·405 (Euler).

100 grams H_2O dissolve 55·8 grams $Pb(NO_3)_2$ at 20° (Le Blanc and Noyes, 1890).

Uses.

1. For explosives.
2. For the manufacture of other lead salts.
3. For fireworks.

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[1] Mulder; Kremers, 1854; at 15°, Michel and Kraft, 1854; at 17° Euler, 1904.

COPPER (CUPRIC) NITRATE, $Cu(NO_3)_2.6H_2O$.

Preparation.

By dissolving copper, copper carbonate, or copper oxide in nitric acid.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$
$$CuCO_3 + 2HNO_3 = Cu(NO_3)_2 + 2H_2O + CO_2$$
$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.$$

Copper (Cupric) Nitrate, $Cu(NO_3)_2 \begin{cases} 3H_2O \text{ above } 24\cdot5^\circ C. \\ 6H_2O \text{ at lower temperature to } -20^\circ C. \\ 9H_2O \text{ below } -20^\circ C. \end{cases}$

Physical Characteristics ($Cu(NO_3)_2.6H_2O$).

Molecular weight	295·69	Melting-point	38°
Specific gravity	2·047	Crystalline form	...

Solubility in Water.[1]

t°	Grams $Cu(NO_3)_2$ per 100 Grams. Solution.	Solid Phase.
−23	36·08	$Cu(NO_3)_2.9H_2O$
−20	40·92	"
−21	39·52	$Cu(NO_3)_2.6H_2O$
0	45	"
+10	48·79	"
18	.53·86	"
20	55·58	"
26·4	63·39	$Cu(NO_3)_2.6H_2O$
25	60·01	$Cu(NO_3)_2.3H_2O$
40	61·51	"
60	64·17	"
80	67·51	"
114·5	77·59	"

Density of solution saturated at 18° = 1·681.

100 grams H_2O dissolve 127·4 grams $Cu(NO_3)_2$ at 20°, d_{20} sat. sol. = 1·688 (Fedotieff, 1911-1912).

Uses.

1. For fireworks.
2. For explosives.
3. As an oxidising agent in calico printing and dyeing.

IRON (FERRIC) NITRATE, $Fe(NO_3)_3.9H_2O$.

Preparation.

By dissolving scrap iron in nitric acid.

$$Fe + 6HNO_3 = Fe(NO_3)_3 + 3H_2O + 3NO_2.$$

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[1] Funk, 1900.

Physical Characteristics.

Molecular weight . . .	404·02	Crystalline form .	Monoclinic . (with $12H_2O$) cubic
Specific gravity . . .	1·684		
Melting-point . . .	47·2°		

Uses.

As a mordant in silk dyeing.

OTHER NITRATES.

Zinc and aluminium nitrates are used to a slight extent in calico printing, and are prepared by dissolving the respective metals in nitric acid.

Basic bismuth nitrate is used in medicine, and is prepared by adding water to the crystalline normal bismuth nitrate prepared by dissolving bismuth in nitric acid.

Other nitrates, used only in chemical laboratory practice, are prepared by general methods (p. 360).

ANALYTICAL.

Detection of Nitric Acid and Nitrates.

1. The addition of copper to nitric acid in any but very dilute solutions, either without or with the application of heat, leads to the formation of brown fumes of nitrogen peroxide.

2. If a solution of indigo is added to nitric acid solution the indigo is decolourised.

3. Ferrous sulphate solution is turned brown by the addition of traces of nitric acid.

4. The most minute traces of nitric acid are detected by the brucine reagent. If to one drop of a solution of 1 part of nitric acid in 200,000 parts of water, one or two drops of a solution of brucine be added and then a few drops of concentrated sulphuric acid, a distinct pink colouration will be observed, if the solution is viewed against a white background.[1] Unless excess of sulphuric acid is present this colouration is also produced with traces of nitrous acid. In order to detect nitric acid apart from nitrous acid, an aqueous solution to be tested

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[1] Reichardt, *Jahresber.*, 1871, p. 893.

should contain at least two-thirds of its volume of strong sulphuric acid. The brucine can be added either as powder or dissolved in pure strong sulphuric acid, say 1 c.c. of a solution of 0·2 gram brucine in 100 c.c. strong acid, for 50 c.c. of the solution to be tested, of which three-fourths must consist of strong sulphuric acid. If as little as $\frac{1}{100}$ mg. of nitric nitrogen be present, a pink colour is produced which gradually, or on heating, very quickly passes through orange to yellow.[1]

5. The diphenylamine reaction is a very delicate one for indicating the presence of minute traces of nitric acid.

The reagent is made by dissolving 0·5 gram diphenylamine in 100 c.c. of pure strong sulphuric acid and adding 20 c.c. of water. The heat produced assists in dissolution. In well-stoppered bottles it keeps for a long time without turning brown. The test for nitrates is carried out by pouring a few cubic centimetres of the heavier liquid into a test-tube. and then adding carefully down the side of the tube the lighter liquid, so that the layers only gradually mix. The presence of as little as $\frac{1}{20}$ mg. of nitrogen as nitrogen acids per litre is indicated by a blue ring forming at the surface of contact of both liquids, most easily perceived by holding the glass sideways against a white background.

This reaction also occurs with nitrous acid, as also do 2 and 3 above.

Nitrates.—The above tests serve for the detection of nitrates when concentrated sulphuric acid is used along with the reagent.

For nitrates, test 2 is usually carried out by mixing a solution of ferrous sulphate with the solution to be tested in a test-tube, and then pouring gently down the side of the tube concentrated sulphuric acid so that it forms a separate layer at the bottom of the tube. A brown ring will form where the two liquids meet in the presence of nitrate.

Alternatively the nitrate solution may be mixed with twice its volume of concentrated sulphuric acid and cooled. On pouring a solution of ferrous sulphate gently on to the surface of the acid liquid, a brown ring forms at the junction of the two layers.

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[1] Lunge, *Sulphuric Acid and Alkali*, Pt. 1, 1, 375.

When heated the brown colouration spreads through the liquid and then disappears.

Estimation of Nitric Acid and Nitrates.

For the estimation of nitric acid and nitrates several well-known and proved methods are available, chief of which are the following:—

1. The nitrometer method due to Lunge[1] (*cf.* pp. 28, 315). It is founded on the reactions:—

$$(a)\ 2HNO_3 + 2Hg_2 + 4H_2SO_4 = 2Hg_2SO_4 + 4H_2O + \underset{\text{nitro-sulphonic acid.}}{2SO_5NH}$$

$$(b)\ 2SO_5NH + Hg_2 + H_2SO_4 = Hg_2SO_4 + \underset{\text{sulphonitronic acid.}}{2SO_5NH_2}$$

$$(c)\ 2SO_5NH_2 = 2H_2SO_4 + 2NO.$$

2. The method of Devarda[2] (*cf.* pp. 31, 391).

It is founded on the reduction of nitric acid to ammonia in alkaline solution by Devarda's alloy (45 parts aluminium, 50 copper, 5 zinc), which is very brittle and easily reduced to a powder.

3. The titration method of Bowman and Scott[3] (*cf.* p. 245).

It depends on the extent of oxidation brought about in a standard ferrous sulphate solution by reduction of nitric acid.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 2NO + 3Fe_2(SO_4)_3 + 4H_2O$$

$$\text{and}\quad 4FeSO_4 + 2HNO_3 + 2H_2SO_4 = N_2O_3 + Fe_2(SO_4)_3 + 3H_2O.$$

The colour produced by the liberated oxide of nitrogen persists when the whole of the nitric acid is decomposed and indicates the end-point of the reaction.

4. Colorimetric estimation by the brucine method.

5. Knecht[4] introduced a rapid method for estimating

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[1] Lunge, *Sulphuric Acid and Alkali*, vol. i. Supp., p. 63.

[2] *Z. anal. Chem.*, 1894, p. 113.

[3] *J. Ind. Eng. Chem.*, 1915, **7**, 766-9.

[4] *J. Soc. Chem. Ind.*, 1915, **34**, 126-7.

nitrates depending on the reducing action of titanous hydroxide, using titanous sulphate or chloride (see p. 244).

$$Ti_2(SO_4)_3 + 6NaOH = Ti_2(OH)_6 + 3Na_2SO_4.$$
$$Ti_2(OH)_6 + 2H_2O = 2Ti(OH)_4 + H_2.$$

Note.—For further particulars in regard to analysis, the reader is referred to Lunge-Keane's *Technical Methods of Chemical Analysis*, under—

Nitric Acid.
Mixed Acids.
Chili Saltpetre ($NaNO_3$).
Nitre (KNO_3).
Calcium Nitrate.
Nitrates.

Notes on Methods of Estimation—(*a*) THE NITROMETER METHOD.—Hill[1] considers the nitrometer method incapable of a high degree of accuracy.

Beckett[2] shows that the nitrometer method of estimating nitrogen in nitro-cellulose invariably yields low results.

The interval of time which is allowed to elapse between the introduction of the nitrate and sulphuric acid into the nitrometer and the shaking has a great influence on the results in the case of nitro-cellulose; with inorganic nitrates the effect is less.

The most trustworthy results are obtained by using 15 c.c. of 92·5 to 94·0 per cent. H_2SO_4, and allowing fifteen minutes to elapse between the introduction of the nitro-cellulose and shaking. In this case the error amounts to about 0·7 per cent. of the nitrogen present.

In a private communication J. S. Hill, outlines a number of errors inherent in the nitrometer method which in careful working amount to about −0·4 per cent. There are errors due to (*a*) side reactions leading to production of N_2O, N_2 and SO_2, (*b*) impurities in the reagents or in the substance analysed, (*c*) solubility of NO in sulphuric acid. In addition, errors of observation in careful working, with calibrated nitrometer (sulphuric acid should be used for calibration), and making all necessary barometric corrections, may amount to ∓0·3 per cent. Hill concludes, "I have no hesitation in

[1] *Analyst*, 1918, **43**, 215-16.

[2] *J. Chem. Soc. Trans.*, 1920, **117**, 220-5.

recommending Devarda's method in preference to the nitrometer method. It is very simple and makes fewer calls for skill on the part of the operator. The nitrometer method is difficult and requires a large amount of skill. It is subject to a constant error, and the errors of observation are at least as great as those of Devarda's method."

Sanders[1] investigated the effect of chlorides on the nitrometer determination of nitrates, and states that chlorides may be present up to 15 per cent. as NaCl without objectionable interference with the nitrate determination.

(*b*) THE DEVARDA METHOD.—Pilz[2] compares estimations of nitrates by various methods, and considers that reduction with Devarda's alloy gives the most trustworthy results.

Erlich[3] describes an apparatus for Devarda's method.

Butt[4] recommends the Devarda method, coupled with the use of a special scrubber bulb designed by Davisson.[5]

Platou[6] considers the Devarda method the most trustworthy method for nitrate estimation in calcium nitrate.

STATISTICS.

Market Prices.

Pre-War Market Prices of Nitrates. (*Average* 1911-13.)

Nitrate.	Price per Ton.					
	As Nitrate.			As Nitrogen.		
	£	s.	d.	£	s.	d.
Ammonium nitrate	35	15	0	102	2	10
Potassium nitrate	24	18	0	179	15	8
Sodium nitrate (95 per cent.) . .	10	13	9	68	10	2
Calcium nitrate	9	15	0	76	9	5

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[1] *J. Ind. Eng. Chem.*, 1920, **12**, 169-70.

[2] *Zeitschr. f. landw. Versuchswesen, Deutschösterr*, 1919, **22**, 180-8; *J. Chem. Soc. Abstr.*, 1920; [II], **118**, 124.

[3] *Ann. Chim. anal.*, 1920, **2**, 143-4; *J. Chem. Soc. Abstr.*, 1920; [II], **118**, 504.

[4] *J. Ind. Eng. Chem.*, 1920, **12**, 352-4; *J. Chem. Soc. Abstr.*, 1920; [II], **118**, 386.

[5] *Ibid.*, 1919, **11**, 465-6; *J. Chem. Soc. Abstr.*, 1919; [II], **116**, 296.

[6] *Chim. et. Ind.*, 1920, **3**, 310-12; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, **39**, 401.

Imports, Exports, Consumption.

Annual Imports, Exports, and Consumption of Nitrates in the United Kingdom—Pre-War Period. (Average 1911-13.)

Nitrate.	Tons.	Totals.
Ammonium Nitrate—		
Imports	1,072	1,072
Potassium Nitrate—		
Imports	11,306	...
Home production	4,819	
		16,125
Exports—		
(1) As potassium nitrate	2,273	...
(2) As explosives (less imports) . . .	3,838	
		6,111
Balance (excess of imports and production over exports)	...	10,014
Balance accounted for—		
(1) Manufacture of explosives for mines and quarries	7,215	...
(2) Manufacture of munitions of war . .	237	...
(3) Manufacture of fireworks . . .	88	...
(4) Balance for rockets and flares exported, meat curing, glass industry, etc. . . .	2,474	
		10,014
Sodium Nitrate (expressed as 95 per cent.)		
Imports	130,997	130,997
Exports—		
(1) As sodium nitrate	10,999	...
(2) As explosives (less imports)	7,648	
		18,647
Balance (excess of imports over exports) . .	...	112,350
Balance accounted for—		
(1) Agriculture	75,000	...
(2) Manufacture of sulphuric acid	18,144	...
(3) Manufacture of nitric acid	4,072	...
(4) Manufacture of potassium nitrate . .	4,264	...
(5) Manufacture of explosives used in mines and quarries	4,041	...
(6) Manufacture of munitions of war . .	4,341	...
(7) Unaccounted for	2,488	...
		112,350
Calcium Nitrate—		
Imports (used in agriculture)	3,600	3,600

From the Final Report, Nitrogen Products Committee, H.M. Stationery Office, 1919.

REFERENCES.

Sodium Nitrate.

PROPERTIES.

BOGORODSKI.—*J. Russ. Phys. Chem. Ges.*, 1905, **37**, 703-59 ; *Chem. Zentr.*, 1905, **2**, 954-5 ; *J. Soc. Chem. Ind.*, 1905, **24**, 1071.

COPPADORO.—*Gazz. Chim. Ital.*, 1912 ; [I], **42**, 233-42 ; *J. Soc. Chem. Ind.*, 1912, **31**, 384.

COPE, U.S. BUREAU OF MINES.—*Met. and Chem. Eng.*, 1916, **15**, 140-3 ; *J. Soc. Chem. Ind.*, 1916, **35**, 944.

WYCKOFF.—*Physical Review*, 1920, **16**, 149-57 ; *J. Chem. Soc. Abstr.*, 1920 ; [II], **118**, 756.

PRODUCTION.

ALLMAND AND WILLIAMS.—*J. Soc. Chem. Ind.* (*Review*), 1919, **38**, 286.

ESTIMATION.

HASKINS AND PHELPS.—*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 66-9 ; *J. Amer. Chem. Soc.* (*Abstr.*), 1921, **15**, 1113.

BUTT.—*J. Ind. Eng. Chem.*, 1920, **12**, 352-4.

DRYING.

PRIDEAUX. —*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 182.

LOWRY AND HEMMINGS.—*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 104.

FOR GUNPOWDER.

39TH ANNUAL REPORT OF H.M.I. OF EXPLOSIVES, 1914.—*J. Soc. Chem. Ind.*, 1915, **34**, 983.

Potassium Nitrate Industry.

OCCURRENCE.

NATTRESS.—*Ann. Rep. Mich. Acad. Sci.*, 1918, **20**, 57-8 ; *J. Amer. Chem. Soc.* (*Abstr.*), 1920, **14**, 2055.

FROOD AND HALL.—*Union of S. Africa Geol. Survey*, 1919, Mem. 14, 1-51 ; *Mineralog. Abstr.*, 1920, **1**, 16 ; *J. Amer. Chem. Soc.* (*Abstr.*), 1920, **14**, 2903.

BRYANT.—*J. Soc. Chem. Ind.* (*Trans.*), 1919, **38**, 360-2.

NITRATES, 1913-1919.—Imperial Mineral Resources Bureau, 28 pp., 9d. ; *J. Soc. Chem. Ind.* (*Review*), 1920, **39**, 417.

NITROGEN PRODUCTS COMMITTEE.—Final Report, 1919, H.M. Stationery Office.

(IN BOLIVIA).—*Comptes rend.*, **99**, 84.

PRODUCTION.

MEYERHOFFER.—*Ber.*, 1904, **37**, 261.

KREMANN AND ZITEK.—*Monatsh.*, 1909, **30**, 311-40 ; *J. Soc. Chem. Ind.*, 1909, **28**, 653.

J. MILBAUER.—*Chem. Zeit.*, 1912, **36**, 331-2 ; *J. Soc. Chem. Ind.*, 1912, **31**, 383.

Hutchinson.—*Agr. Res. Inst.*, Pusa, India, Bull. No. 68; *Nature*, 1917, **99**, 447-8.

Anon.—*Bol. soc. fomento. fabril* (Chili), 1918, **35**, 116-17; *J. Amer. Chem. Soc.* (*Abstr.*), 1919, **13**, 2257.

Barton.—*Chem. and Met. Eng.*, 1918, **18**, 248.

Kippenberger.—*Ber. Pharm. Ges.*, 1919, **29**, 391-405.

Gale.—*Eng. and Min. J.*, 1919, **107**, 1025-31; *J. Amer. Chem. Soc.* (*Abstr.*), 1919, **13**, 1903; *Eng. and Min. J.*, 1919, **107**, 385-8; *J. Amer. Chem. Soc.* (*Abstr.*), 1919, **13**, 891.

Holstein.—*J. Ind. Eng. Chem.*, 1920, **12**, 290-3.

Nitrates, 1913-1919.—Imperial Mineral Resources Bureau, 28 pp., 9d.; *J. Soc. Chem. Ind.* (*Review*), 1920, **39**, 417; Nitrogen Products Committee, Final Report, H.M. Stationery Office.

Potassium Nitrate.

ESTIMATION.

Wogrinz and Kuber.—*Chem. Zeit.*, 1919, **43**, 21-2; *J. Chem. Soc.* (*Abstr.*), 1919; [II], **116**, 167.

PROPERTIES.

E. Groschuff.—*Ber.*, 1904, **37**, 1486-93; *J. Soc. Chem. Ind.*, 1904, **23**, 505.

J. Herbette.—*Comptes rend.*, 1906, **143**, 128-30; *J. Soc. Chem. Ind.*, 1906, **25**, 757.

Bogorodski.—*J. Russ. Phys. Chem. Ges.*, 1905, **37**, 703-59; *Chem. Zentr.* 1905, **2**, 954-5; *J. Soc. Chem. Ind.*, 1905, **24**, 1071.

Findlay, Morgan, and Morris.—*J. Chem. Soc. Trans.*, 1914, **105**, 779-82.

Cope, U.S. Bureau of Mines.—*Chem. and Met. Eng.*, 1916, **15**, 140-3; *J. Soc. Chem. Ind.*, 1916, **35**, 944.

Lowry and Hemmings.—*J. Soc Chem. Ind.* (*Trans.*), 1920, **39**, 104.

DRYING.

Prideaux.—*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 182-5.

Ammonium Nitrate—Manufacture, etc.

Le Chatelier and Bogitch.—*Comptes rend.*, 1915, **161**, 475-9; *J. Soc. Chem. Ind.*, 1915, **34**, 1141.

Rengade.—*Rev. gén. des Sciences*, 1917, **28**, 489-503; *J. Amer. Chem. Soc.* (*Abstr.*), 1918, **12**, 1026.

Scott.—*Chem. News*, 1917, **116**, 175-8, 187-9.

Bolling.—*Chem. and Met. Eng.*, 1919, **20**, 401-5; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, **38**, 359.

U.S. Plant at Perryville.—*Chem. and Met. Eng.*, 1919, **20**, 320-6.

Muscle Shoals Plant.—*Met. and Chem. Eng.*, 1920, **22**, 417-9.

Garelli.—*J. Ind. Eng. Chem.*, 1920, **12**, 390.

ECONOMICS.

Diefenbach.—*Chem. Ind.*, 1914, **37**, 265-9.

TABLES FOR PREPARATION OF SOLUTIONS.

Gautsch.—*Chem. Zeit.*, 1916, **40**, 1049-50; *J. Soc. Chem. Ind.*, 1917, **36**, 135.

PURIFICATION.

RENGADE.—*Comptes rend.*, 1917, **165**, 237-40; *J. Soc. Chem. Ind.*, 1917, **36**, 961.

ANALYSIS.

WOGRINZ AND KUBER.—*Chem. Zeit.*, 1919, **43**, 21-2; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, **38**, 173.

LADD.—*J. Ind. Eng. Chem.*, 1919, **11**, 552-5; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, **38**, 498.

J. T. GRISSOM.—*J. Ind. Eng. Chem.*, 1920, **12**, 172-3; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, **39**, 332.

PROPERTIES.

COPE, U.S. BUREAU OF MINES.—*Met. and Chem. Eng.*, 1916, **15**, 140-3; *J. Soc. Chem. Ind.*, 1916, **35**, 944.

GROSCHUFF.—*Ber.*, 1904, **37**, 1486-93; *J. Soc. Chem. Ind.*, 1904, **23**, 505.

DRYING.

PRIDEAUX.—*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 182-5.

LOWRY AND HEMMINGS.—*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 102-4.

FREEZING POINT.

EARLY AND LOWRY.—*J. Chem. Soc. Trans.*, 1919, **115**, 1387-1408.

AS FERTILISER.

RUSSELL.—*J. Bd. Agric.*, 1919, **25**, 1332-9; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, **38**, 228.

EVAPORATION.

PRIDEAUX AND CAVEN.—*J. Soc. Chem. Ind.* (*Trans.*), 1919, **38**, 353-5.

HEATS OF DILUTION.

PRATT.—*J. Franklin Inst.*, 1918, **185**, 663-95; *J. Amer. Chem. Soc.* (*Abstr.*), 1918, **12**, 1436.

Calcium Nitrate.

SOLUBILITIES.

CAMERON AND ROBINSON.—*J. Phys. Chem.*, 1907, **11**, 273-8; *J. Soc. Chem. Ind.*, 1907, **26**, 1197.

BASSETT AND TAYLOR.—*J. Chem. Soc. Proc.*, 1912, **28**, 48; *J. Chem. Soc. Trans.*, 1914, **105**, 1926-41.

PRODUCTION.

NITROGEN PRODUCTS COMMITTEE.—Final Report, H.M. Stationery Office.

MUNTZ AND LAINÉ.—*Comptes rend.*, 1905, **141**, 861-7; *J. Soc. Chem. Ind.*, 1905, **24**, 1301; *Comptes rend.*, 1906, **142**, 430-5; *J. Soc. Chem. Ind.*, 1906, **25**, 275.

Barium Nitrate.

DECOMPOSITION.

B. N. GOTTLIEB.—*Chem. Zeit.*, 1904, **28**, 356; *J. Soc. Chem. Ind.*, 1904, **23**, 545.

SOLUBILITIES.

PARSONS, CORSON, PERKINS.—*J. Amer. Chem. Soc.*, 1910, **32**, 1383-9; *J. Soc. Chem. Ind.*, 1910, **29**, 1375.

COPPADORO.—*Gaz. Chim. Ital.*, 1912; [I], **42**, 233-42; *J. Soc. Chem. Ind.*, 1912, **31**, 384.

FINDLAY, MORGAN, AND MORRIS.—*J. Chem. Soc. Trans.*, 1914, **105**, 779-82.

STRUCTURE.

NISHIKAWA AND HUDINUKI.—*Proc. Tokyo Mathematico-Phys. Soc.*, 1917; [II], **9**, 197; *J. Amer. Chem. Soc.* (*Abstr.*), 1917, **11**, 3170.

Strontium Nitrate.

SOLUBILITIES.

PARSONS, CORSON, PERKINS.—*J. Amer. Chem. Soc.*, 1910, **32**, 1383-9; *J. Soc. Chem. Ind.*, 1910, **29**, 1375.

FINDLAY, MORGAN, AND MORRIS.—*J. Chem. Soc. Trans.*, 1914, **105**, 779-82.

MANUFACTURE.

IRVIN.—*Mining Sci. Press*, 1916, **113**, 774-6; *J. Amer. Chem. Soc.* (*Abstr.*), 1917, **11**, 388.

NISHIKAWA AND HUDINUKI.—*Proc. Tokyo Mathematico-Phys. Soc.*, 1917; [II], **9**, 197; *J. Amer. Chem. Soc.* (*Abstr.*), 1917, **11**, 3170.

Silver Nitrate.

PROPERTIES.

BAILAR.—*Western Chem. and Met. Mining World*, Chicago, 13th Aug. 1910; *J. Soc. Chem. Ind.*, 1910, **29**, 1085.

LUDWIG.—*Bull. Soc. chim. Roumania*, 1920, **2**, 28-32; *J. Amer. Chem. Soc.* (*Abstr.*), 1920, **14**, 3614.

PREPARATION.

WARDEN.—*Pharm. J.*, 1897; [1387], **58**, 61; *J. Soc. Chem. Ind.*, 1897, **16**, 255.

GRUENER.—*J. Amer. Chem. Soc.*, 1910, **32**, 1030-2; *J. Soc. Chem. Ind.*, 1910, **29**, 1155.

ROSA, VINAL, AND M'DANIEL.—*Bull. Bureau of Standards*, 1913, **9**, 524-51; *J. Soc. Chem. Ind.*, 1914, **33**, 482.

DECOMPOSITION.

DIVERS.—*J. Chem. Soc. Trans.*, 1899, **75**, 83.

Copper Nitrate.

DRYING.

LOWRY AND HEMMINGS.—*J. Soc. Chem. Ind.* (*Trans.*), 1920, **39**, 102.

Iron (Ferric) Nitrate.

PREPARATION.

MOYRET.—*J. Soc. Chem. Ind.*, 1882, **1**, 149.

Aluminium Nitrate.

STILLMAN.—*J. Amer. Chem. Soc.*, 1897, **19**, 711-16.
FRIEND.—*A Text-book of Inorganic Chemistry*, Vol. IV., 1917.

HYDRATES.

JOVITSCHITSCH.—*Monatsh.*, 1912, **33**, 9-18; *J. Soc. Chem. Ind.*, 1912, **31**, 186.
SELIGMAN AND WILLIAMS.—*J. Chem. Soc. Trans.*, 1916, **109**, 612-17.
INAMURA.—*J. Tokyo Chem. Soc.*, 1920, **41**, 1-8; *J. Chem. Soc. Abstr.*, 1920; [II], **118**, 625.

Nitrates (General).

SOLUBILITIES.

FUNK.—*Ber.*; [I], **32**, 96-106; *J. Soc. Chem. Ind.*, 1899, **18**, 273.
PRATT.—*J. Franklin. Inst.*, 1918, **185**, 663-95; *J. Amer. Chem. Soc. Abstr.*; 1918, **12**, 1436.

CONSTITUTION.

SCHÆFFER.—*Z. wiss. Photochem.*, 1918, **17**, 193-217; *J. Chem. Soc.* (*Abstr.*), 1918; [II], **114**, 254.

REDUCTION.

MÜLLER AND SPITZER.—*Ber.*, 1905, **38**, 1190-4; *J. Soc. Chem. Ind.*, 1905, **24**, 445.

FOR GLASS MANUFACTURE.

SPRINGER.—*Sprechsaal*, 1914, **47**, 361-3; *J. Soc. Chem. Ind.*, 1914, **33**, 693.

PRODUCTION.

NITROGEN PRODUCTS COMMITTEE.—Final Report, H.M. Stationery Office, 1919, 4s.

PATENTS

Manufacture of Potassium Nitrate.

Soc. "Le Nitrogène" (Fr. P. 400958, 18th March 1909). For the separation of the mixture of nitrate and nitrite formed by the absorption of oxides of nitrogen, from mixtures of these with air, by milk of lime, the neutral solution is treated with potassium and sodium sulphates or carbonates, in such quantities that the potassium salt is equivalent to the nitrate and the sodium salt to the nitrite present; after separation of the precipitated calcium sulphate or carbonate, the potassium nitrate and sodium nitrite are obtained from the solution by successive crystallisations. The potassium and sodium salts may also be added before absorption of the oxides of nitrogen by the lime; or, the same end may be reached by using for the absorption a mixture of sodium and potassium hydroxides, or such of their salts as are decomposed by nitrous and nitric acids, in the proportion in which nitrite and nitrate respectively are subsequently produced.

Freeth and Cocksedge (B. P. 124513, 25th February 1916). Crude sodium nitrate containing potassium salts is digested with sufficient water or liquor from a previous extraction, to dissolve the potassium salts and to yield a solution saturated or nearly saturated with the potassium salts. The temperature of digestion should be as high as practicable. The solution is separated from the undissolved sodium nitrate at the temperature of digestion, and, if saturated with potassium salts, it is diluted with sufficient water to keep the sodium nitrate in solution at the temperature to which the solution is to be cooled; it is then cooled to the desired temperature, when pure potassium nitrate crystallises out. If the solution is not saturated with potassium salts, it is concentrated until it is saturated at a high temperature, *e.g.*, 100° C., and after removal of any sodium nitrate which crystallises out, it is treated as before.

Bailey, Denny, and Jeffries (B. P. 124960, 5th June 1918). Potassium nitrate is separated from crude sodium nitrate by leaching with a solution containing both nitrates of a determined composition, cooling the solution to separate mixed nitrates, dissolving out the sodium nitrate together with some potassium nitrate from the mixed nitrates, and using the mother liquor and the liquor produced in the second operation to treat more crude nitrate. The sodium nitrate left after the first operation and the potassium nitrate obtained by the washing of the deposited nitrates are washed with saturated solution of sodium and potassium nitrates respectively. Any perchlorate present is decomposed by fusing the nitrate.

Detwiller (U.S. P. 1274145, 30th July 1918). Powdered alunite is agitated with boiling nitric acid, residual SiO_2 is separated by filtration, ammonia, caustic potash, or other alkali is added to the filtrate with constant agitation, and the precipitated alumina thus formed is recovered by filtration. The second filtrate is treated with powdered $BaCO_3$ with agitation and boiling, and precipitated $BaSO_4$ is recovered by filtration. The filtrate obtained from this step is treated with HNO_3 and the KNO_3 formed is crystallised.

Given and Barteaux (U.S. P. 1294788, 18th February 1919). A solution containing nitrates of both sodium and potassium is evaporated in vacuo at a temperature of about 80 to 95° C. until some $NaNO_3$ is separated, and the KNO_3 is then separated from the concentrated solution remaining.

Fairbrother (B. P. 135713, 20th February 1919). Potassium is recovered as nitrate from the waste gases of cement kilns and the like by bringing the gases into intimate contact with a solution of a metal nitrate, preferably $NaNO_3$. The K_2O and CO_2 in the gases interact with the $NaNO_3$ to form KNO_3 and Na_2CO_3, hydrosilicates being also produced from the silicates present in the gases. The hydrosilicates are rendered insoluble by heating the solution, leaving the KNO_3 and Na_2CO_3 to be separated by crystallisation. A suitable construction is specified.

Fairbrother (B. P. 135720, 24th February 1919). Hot gases from a cement kiln are passed through two towers in series, through which water or an aqueous solution of sodium, potassium, or aluminium silicates is also circulated by a pump and spray nozzles. The cement dust and about 50 per cent. of the potassium oxide are extracted, and the gas is then passed through a conduit centrifugal fan and two additional towers in series, through which sulphuric, hydrochloric, boric, or nitric acid is circulated. The potassium is extracted as a substantially pure salt from the liquor in the store tank. The slurry from the first pair of towers is collected from the tank and treated for the recovery of the potassium compounds.

Blumenberg (U.S. P. 1296460, 4th March 1919). Gases containing potassium compounds and cement dust in suspension are passed through a solution of a metallic nitrate, *e.g.*, sodium nitrate, the solution being afterwards evaporated to dryness to render the silicates insoluble. Potassium nitrate is then extracted from the product with water.

Blumenberg (U.S. P. 1297640, 18th March 1919). In obtaining KNO_3 from refractory silicate materials such as feldspar, cement dust, phonolite tailings, lepidolite, or similar substances, the material is calcined (at about 815° C. in the case of feldspar), preferably dropped into water while hot to facilitate disintegration, ground to 100 to 200 mesh, and then heated with $NaNO_3$ (to about 535° C. in the treatment of feldspar) to effect double decomposition. KNO_3 may be thus obtained in an amount equal to 65 to 80 per cent. of the theoretical yield. Extraction of the KNO_3 is preferably effected by boiling the reaction products with water under 4 to 5 atmospheres' pressure. The excess of SiO_2 and Al_2O_3 present remain as an insoluble residue. The reaction with $NaNO_3$ usually requires six to eight hours for its completion and is facilitated by use of an excess of $NaNO_3$.

Freeth (U.S. P. 1300947, 15th April 1919). Potassium nitrate is extracted from crude sodium nitrate in hot aqueous solution, the solution is separated from undissolved sodium nitrate, and the composition of the solution is so adjusted by dilution that on cooling to a temperature which may be about 20° C., it will deposit a considerable amount of potassium nitrate without depositing sodium nitrate, and the solution is then cooled to effect this separation.

E. Hene and A. van Haaren (Ger. P. 332002, 14th April 1920). Crude calcium cyanamide, potassium sulphate, nitric acid, and water are stirred together at a temperature below 100° C., preferably 25° to 35° C., and the liquor filtered.

Badische Anilin- und Soda-Fabrik (Ger. P. 306334, 11th March 1916). Ammonium nitrate and potassium chloride are dissolved in hot water; potassium nitrate crystallises on cooling, and a mixed salt, suitable for use as a fertiliser, is separated from the mother liquor either by evaporation to dryness or by fractional crystallisation. If the potassium chloride employed contains much sodium chloride, the quantity of water is so adjusted that the greater part of the sodium chloride remains undissolved in the hot solution.

Badische Anilin- und Soda-Fabrik (Ger. P. 307112, 18th April 1916, addition to 306334). The solution, after separating most of the potassium nitrate, is concentrated slightly, moderately cooled to deposit ammonium chloride, and filtered. To render the process continuous, limited quantities of potassium chloride, ammonium nitrate, and water are added to the residual liquor, and the latter is again subjected to the process. For example, to 72 parts of a solution containing 16 parts each of potassium nitrate and ammonium chloride and 40 parts of water, there are added 28 parts of water, 8 parts of ammonium nitrate, and 7.5 parts of potassium chloride. After dissolving the added salts by heating to 30° to 40° C., potassium nitrate is separated by cooling to 0° C., then 27 to 28 parts of water is evaporated from the mother liquor, and the residual solution cooled to 20° C., whereupon pure ammonium chloride separates.

Badische Anilin- und Soda-Fabrik (Ger. P. 310601, 8th November 1920, addition to 306334). By cooling a hot solution of 98.5 per cent. ammonium nitrate, 204 parts; 98.7 per cent. potassium chloride, 206 parts; and water, 425 parts, to 2° C., 165 parts of 99 per cent. potassium nitrate is recovered. On evaporating the mother liquor a mixture is obtained which contains about 36 per cent. of potassium nitrate, 55 per cent. of ammonium chloride, 8 per cent. of potassium chloride, and 1 per cent. of sodium chloride, and which has good keeping properties in a moist atmosphere.

Coe and Dorr Co. (U.S. P. 1292580, 1st January 1919). Crude material containing nitre is treated at about 50 to 70° C. in a solution which is saturated when cold both with nitre and with the soluble impurities (chiefly NaCl). The solution dissolves more nitrate but very little more sodium chloride. On cooling, impure nitre separates. This is then digested at 100 to 120° C. with a solution which, when cool or moderately warm, is saturated with both nitre and impurities, whereby the nitre is dissolved but not the impurities, and some of the impurities already in solution are precipitated. On cooling the resultant solution commercially pure nitrate separates.

Manufacture of Ammonium Nitrate.

Fairley[1] discusses the processes proposed and patented for the production of ammonium nitrate for explosives purposes.

"Generally it (ammonium nitrate) has been made by neutralising nitric acid by means of ammonia, and usually the liquid acid is saturated with ammonia gas, but in Hake's patent (B. P. 11731, 14th August 1888) both the constituents are mixed in the state of vapour. Very fine salts may be obtained by such processes, but more costly than if the salt could be obtained by the double decomposition of the cheapest nitrate—sodium nitrate.

"Little difficulty has been found in carrying out the manufacture of the corresponding potassium salt by the reaction of KCl, K_2CO_3, or KOH on sodium nitrate.

"The very great solubility of ammonium nitrate in water has, however, hitherto proved a difficulty in its manufacture by similar means, especially as the presence of 1 or 2 per cent. of fixed impurity renders the salt unfit for a "safety" explosive.

"The development of the ammonia soda process suggested its application to sodium nitrate instead of sodium chloride.

$$\underbrace{NH_3.H_2O.CO_2} + NaNO_3 = NaHCO_3 + NH_4NO_3.$$

"In 1875 Gerlach[2] patented processes based on this reaction in England and in Germany, having special reference to the purification of gas liquor. Lesage and Co. in 1877 and Chance,[3] in this country in 1885, also took out patents for the application of the ammonia soda process to sodium nitrate (B. P. 5919, May 1885).

"Other processes depending on the solubility of ammonium nitrate in alcohol, and the use of this solvent to extract the salt from the products of double decomposition have been proposed by:—

1889, Roth (B. P. 1885, Ger. P. 48705); 1889, Wahlenburg (B. P. 12451); 1892, Groendahl and Landin (B. P. 1868).

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[1] *J. Soc. Chem. Ind.*, 1897, **16**, 211-13.

[2] *Dingl. polyt. J.*, **228**, 82-90; *J. Chem. Soc.*, 1877, **32**, 236-86.

[3] *J. Soc. Chem. Ind.*, 1886, **5**, 325.

"In these processes the ammonium salts (generally sulphate) are treated with sodium nitrate in various ways and the products extracted with alcohol."

Fairley proceeds to show that the ammonium nitrate produced by any of the above methods contains about 10 per cent. of sodium nitrate, and patents an improved method (B. P. 1668, 23rd January 1896) in which he washes the crude ammonium nitrate with pure ammonium nitrate solution and gets a product containing only 1 per cent. of impurity.

E. Naumann (Ger. P. 166746) promotes the old reaction between ammonium sulphate and sodium nitrate by separating the sodium sulphate formed from the mother liquor while still hot; the solution is then cooled to the point where only a double sulphate of ammonium and sodium crystallises out, and the mother liquor, on concentration and cooling, yields solid, nearly pure, ammonium nitrate.

Garroway (B. P. 7066, 18th March 1897). Sodium nitrate or potassium nitrate, mixed with silica in the form of sand or ground flints, is passed through a valved hopper into a muffle furnace, heated externally, to which superheated steam is admitted. The mixture is carried forward by arms and discs attached to a revolving shaft for delivery at the opposite end of the furnace, so as to make the process continuous. The nitric acid vapours evolved are taken, first to a condenser in which a portion of the acid collects, and then through a series of towers, fitted with baffle plates, to the first of which ammonia gas is admitted. The residual vapours are passed through a tower, where any excess of ammonia is neutralised by a sulphuric acid spray. The ammonium nitrate solution formed in the condensing towers is drawn off, and concentrated in enamelled cast-iron pans, to obtain the solid salt. The alkali silicate formed may be either utilised as such, or it may be treated in solution with lime to obtain caustic soda or potash, and a residue of calcium silicate, available in the manufacture of cement, etc. Refer to B. P. 2489 of 1896.

Garroway (B. P. 22395, 30th September 1897). A constant stream of nitric acid is produced by heating a mixture of silica and sodium nitrate in a suitable furnace, in a current of superheated steam as described in B. Ps. 2489 of 1896 and 7066 of 1897. The residue of sodium silicate may be used as such, or it may be treated with limewater to obtain caustic soda in solution, and a residue of silicate of lime available as a cement. The nitric acid is led, as produced, into earthenware pipes or stone towers, in which it is brought into contact with scrap lead or litharge. The lead nitrate solution formed, after neutralisation with ammonia, is treated under pressure with ammonia and carbonic acid, or with ammonium carbonate, to obtain lead carbonate and ammonium nitrate. The ammonium carbonate for effecting the precipitation may be obtained by decomposing ammonium sulphate with barium carbonate, which process is included in the claims.

Kynaston (B. P. 10137, 13th May 1899). When a solution of sodium nitrate and strontium chloride, in which the salts are present in equivalent quantities, is boiled down, a large proportion of the sodium separates as sodium chloride, while the equivalent quantity of strontium nitrate remains in solution, and if this solution, while still hot, be drawn off, it yields on cooling crude strontium nitrate containing from 85 to 90 per cent. $Sr(NO_3)_2$ and 10 to 15 per cent. of other salts in admixture.

Further purification is effected by recrystallisation. To a solution of the pure strontium nitrate thus obtained, a solution of ammonium sulphate is now added so as to exactly precipitate the strontium present, with the consequent production of a solution of ammonium nitrate, which is drawn off, concentrated, and allowed to crystallise. The deposited strontium sulphate is converted by means of sodium carbonate into strontium carbonate, which in its turn is dissolved in hydrochloric acid yielding strontium chloride once more for the first operation. The solution of sodium sulphate is concentrated by evaporation, and yields, on cooling, crystals of Glauber's salt.

Garroway (B. P. 10137, of 1899) first obtains strontium nitrate from sodium nitrate and strontium chloride (most of the NaCl separating out on cooling), and after purifying it by recrystallisation, adds the exactly equivalent quantity of ammonium sulphate. The latter is thus converted into nitrate and remains in solution. All the strontium is precipitated as sulphate, which is converted into carbonate by means of sodium carbonate, and from the $SrCO_3$ the $SrCl_2$ is again prepared by means of hydrochloric acid. Carez (Ger. P. 42178) proceeds in the same way with barium chloride.

Ostwald (B. Ps. 698 and 8300, of 1902; 7909, of 1908; U.S. P. 858904), with the co-operation of Brauer, found as best catalyser for the oxidation of ammonia platinum foil, covered with platinum black, which allows of utilising gaseous mixtures containing but a small percentage of ammonia. Gas-liquor, putrefied sewage, etc., are mixed with a sufficient quantity of caustic lime or soda, and treated with air on the counter-current principle. There must be at least 7O for $2NH_3$, to produce $2NO_2 + 3H_2O$. The gaseous current must have a certain rate of speed, and the contact mass a temperature over 300°. The nitric acid formed is obtained as ammonium nitrate. Ostwald's process has been carried out on a large scale by the Gewerkschaft Lothringen at the Mont Cenis coal-pit.

Naumann (Fr. P. 339733, 20th January 1904). A mixture of solutions of sodium nitrate and of ammonium sulphate is boiled, and the sodium sulphate which salts out is removed. At a certain stage of the process the solution is cooled sufficiently to become saturated with ammonium nitrate; a double salt containing ammonium sulphate then separates, and the mother liquor, after concentration if desired, is rapidly cooled in a prescribed manner, not subject to external disturbance, to obtain a deposition of ammonium nitrate, which may be refined.

J. Rudeloff (Ger. P. 166427, 4th September 1904). In the denitration of the spent acid from the nitration of glycerine, cellulose, etc., the mixed acid is heated in a suitable vessel, and the nitric acid vapours are expelled by steam or hot air. It is found that these vapours may be suitably utilised for the manufacture of ammonium nitrate. The hot vapours are treated with ammonia solution, and the resulting solution of ammonium nitrate is concentrated in pans heated by the residual sulphuric acid from the denitrating apparatus. The ammonium nitrate is then separated by crystallisation.

Wedekind und Co., G.m.b.H. (Fr. P. 369389, 31st August 1906; B. P. 19465, 31st August 1906); Caspari and Nydegger and Wedekind und Co. (U.S. P. 864513, 27th August 1907). An aqueous solution containing ammonium sulphate and an excess of sodium nitrate is evaporated until it has become saturated with ammonium nitrate at a temperature of 50 C. or over. Most of the sodium sulphate crystallises out during the evaporation, together with some sodium nitrate. The solution is cooled until the separation of ammonium nitrate commences (the solution becomes turbid), and then sufficient water is added to the mother liquor to let the ammonium nitrate crystallise out free from sodium salts, when the liquid cools to the ordinary temperature.

According to the German patent of the Norsk Hydro-Elektrisk Kvaelstofaktieselskab, No. 206949, of 1907, ammonium nitrate is obtained, together with calcium nitrate, by absorbing nitrous vapours by calcium cyanamide, the reaction taking place quite smoothly according to this equation:—

$$CaCN_2 + 2H_2O + 4HNO_3 = Ca(NO_3)_2 + CO_2 + 2NH_4 . NO_3.$$

Dyes (B. P. 15391, 1908) adds to a solution of calcium nitrate a solution of ammonium sulphate, so that calcium sulphate is precipitated.

Nydegger and Wedekind und Co. (B. P. 20907, 13th September 1909; U.S. P. 986204, 7th March 1911). The double decomposition of ammonium sulphate and commercial calcium (or strontium or barium) nitrate, containing magnesium compounds, is effected in the presence of an excess of the latter salt, preferably 1 to 10 per cent. above the theoretical quantity; ammonium nitrate, free from magnesium, is thus obtained by concentrating the solution, and the mother liquor, containing the magnesium and excess of calcium salt is added to fresh solutions of the decomposed salts before evaporation, until it becomes necessary to remove the accumulated magnesium salts; this is done by adding sufficient ammonium sulphate to convert the soluble calcium and magnesium salts into sulphates and leave an excess preferably 1 to 10 per cent. (of the ammonium nitrate present); the alkaline-earth sulphate and magnesium sulphate, or its double salt with ammonium sulphate, are thus in large measure precipitated, and after adding a fresh excess of alkaline-earth nitrate, the solution is returned to the concentrating vessel.

Plantz (Ger. P. appl. P30765) gives directions for obtaining pure ammonium nitrate from crude calcium nitrate ("Norgesalpeter").

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Fr. P. 408506, 2nd November 1909). Solutions of calcium nitrate and ammonia are mixed, in any desired proportion, and the mixture is treated with carbonic acid; calcium carbonate is thereby precipitated and ammonium nitrate obtained in solution.

Freeth and Cocksedge (B. P. 16455, 9th July 1910; U.S. P. 1051097, 21st January 1913). Sodium nitrate, ammonium bicarbonate, (or its components) and water are made to react at any temperature at which the substances will form ammonium nitrate (preferably below 35° C.) and in such quantities as will yield, when the reaction is finished and the precipitated sodium bicarbonate has been removed at the temperature of the reaction, a solution saturated with respect to sodium bicarbonate and also saturated, or nearly saturated, with respect to ammonium bicarbonate and ammonium nitrate. The solution, after removal of the sodium bicarbonate, is then treated so as to get rid of all or most of the bicarbonate remaining in solution (for instance, by heating at or below atmospheric pressure), and is subsequently cooled to a temperature below that at which the reaction was performed (as low as −25° C. if desired), when pure or practically pure ammonium nitrate separates. Equivalent quantities of ammonium bicarbonate and sodium nitrate, the latter in such quantity that it is equivalent to the ammonium nitrate which has been removed by cooling, are then added to the mother liquor (small adjustments being made to compensate for losses during the process of removing the soluble bicarbonates, for addition of washwater, etc.), and the cycle of operations is repeated. As an example, 200 parts by weight of sodium nitrate, 210 parts of ammonium bicarbonate, and 100 parts of water are stirred together at any temperature between 33° and 22° C., and, when the reaction is finished, the precipitated sodium bicarbonate is separated from the solution at 22° C. The remaining solution is then heated to remove the soluble bicarbonate and is subsequently cooled. At - 1° C. about 55 parts of ammonium nitrate are obtained, per 100 parts of water, or about 100 parts by cooling to - 22° C.

Electrochem. Werke, G.m.b.H. (Ger. P. 233895, 17th July 1910; B. P. 16426 of 1911; Fr. P. 432252, 13th July 1911). The process consists in electrolysing aqueous nitric acid of less than 30 per cent. concentration at the ordinary temperature, using an aluminium cathode, and a solution of nitric peroxide or nitrous acid in dilute nitric acid as anode liquid. The current density may vary within wide limits, but it is essential to work at the ordinary temperature and with acid of the concentration mentioned; otherwise loss of nitrogen occurs. The oxygen formed at the anode serves to oxidise the lower oxides of nitrogen to nitric acid, and in order that it may not interfere with the reduction process at the cathode, a diaphragm is used to separate the anode and cathode compartments.

Other patents on electrolytic production are:—

Farbwerke vorm Meister, Lucius, and Brüning (Ger. P. 238137; Fr. P. 433410).

Siemens and Halske (Ger. P. 85103) prepare ammonium nitrate from gaseous ammonia by the silent discharge.

Henry (B. P. 19141, 15th August 1910). Calcium (barium or strontium) nitrate and ammonium sulphite solutions (preferably concentrated) are mixed in about equivalent quantities, and, after separating from the precipitated calcium sulphite and removing any remaining calcium, if desired, by adding the calculated quantity of ammonium oxalate, the solution is evaporated until it has a boiling-point of 125° C. and is then cooled to about 30 to 40° C., when a large proportion of the ammonium nitrate crystallises in a very pure state.

Knab (Fr. P. 116331) treats alkaline nitrates with ammonium oxalate.

Traine and Hellmers, and Weyer (Ger. P. 254935, 11th April 1911). A mixture of calcium nitrate with excess of ammonium sulphate, with or without addition of water, is heated under ordinary or increased pressure until the water is completely expelled and the mass is fused. The product, after cooling, is broken up and treated with a suitable organic solvent, *e.g.*, alcohol, to extract the ammonium nitrate. It is stated that ammonium nitrate of about 99.9 per cent. purity can be obtained directly in this way.

Freeth and Cocksedge (Ger. P. 256335) agitate equivalent quantities of ammonium sulphate and sodium nitrate with a hot solution previously saturated in the cold state with ammonium nitrate and sodium nitrate, and then with sodium sulphate, until the double salt of ammonium nitrate and ammonium sulphate begins to crystallise out, or with mother liquors of the same composition, and evaporate the mixture as long as only sodium sulphate separates out; after removing this, the solution is mixed with water and cooled up to the point where ammonium nitrate crystallises out. Their Ger. P. 271518 describes the production of ammonium nitrate from sodium nitrate and ammonium bicarbonate or its components, employing such proportions that at the end of the reaction, besides the precipitated sodium bicarbonate, a solution remains, saturated at the temperature of the reaction with sodium bicarbonate, ammonium bicarbonate, and nitrate; after removing the bicarbonates, the solution is cooled down and the ammonium nitrate now falling out is separated and washed in the usual manner. The most suitable temperature for the reaction is below 35°.

Naumann (Ger P. 259995, 16th May 1911). The mixture of ammonium nitrate and ammonium-sodium sulphate obtained in the fractional crystallisation and by strong cooling of the mother liquors is mixed with hot mother liquors relatively poor in ammonium nitrate under such conditions that a solution saturated with ammonium nitrate at 25° to 55° C. is obtained. From this, after removal of the separated double salt of ammonium sulphate and nitrate, ammonium nitrate is recovered by cooling to the ordinary temperature, with or without addition of water. The double salt of ammonium sulphate and nitrate may be used in place of, or in addition to, the mixture of ammonium nitrate and ammonium-sodium sulphate; but in this case the treatment is first effected at 75° C., at which temperature the double salt of ammonium sulphate and nitrate is decomposed. After removal of the separated ammonium sulphate, the further treatment is as described above.

Electrochem. Werke, G.m.b.H. (B. P. 16426, 17th July 1911; Fr. P. 432252, 13th July 1911). Nitric acid containing less than 30 per cent. of HNO_3 and containing also some 5 per cent. of ammonium nitrate is electrolysed at the ordinary temperature in a diaphragm cell with an aluminium cathode. In the anode compartment is a mixture of nitrous acid and nitric acid, or solution of nitrogen oxides in nitric acid, which is converted into nitric acid by the anodic oxygen. Fresh nitric acid is added to the cathode compartment as the electrolysis proceeds, till the liquid contains about 40 per cent. of ammonium nitrate, and the process is continued till the cathode liquid is neutralised.

Uhde (Fr. P. 436768, 28th October 1911; U.S. P. 1053456, 18th February 1913). The process described in Fr. P. 417505, of 1910, is modified by (1) the employment of uncooled gases, without previous dehydration, the temperature of the absorbing liquid being maintained at about 100° C.; (2) the use of concentrated ammoniacal gases, such as are obtained from ammoniacal liquors; and (3) the treatment of the liquor obtained, by slightly acidifying and heating until a reaction commences (with a slight evolution of gas) so as to give a product which is chemically pure.

Collett and Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. P. 26097, 13th November 1912; U.S. P. 1058037, 8th April 1913). The production of ammonium phosphate is combined with that of ammonium nitrate by dissolving calcium phosphate, insoluble in water, in dilute nitric acid, adding ammonium sulphate in such proportion that the calcium is precipitated as sulphate, and treating the solution, which contains substantially only ammonium phosphate and nitrate, in any suitable manner, as, for example, by neutralising with ammonia and fractionally crystallising.

Wülfing, Dahl und Co. (Fr. P. 465683 18th November 1913; B. P. 26233, 15th November 1913). Sodium nitrate (1 molecule), or a mixture containing alkali nitrate and other alkali or ammonium salts, is treated in aqueous solution with sufficient ammonium sulphate (at least 1 molecule) to convert all the alkali metal into alkali ammonium sulphate, and the ammonium nitrate formed is separated by fractional crystallisation from the less soluble double salt, or the solution is concentrated and extracted with alcohol or other solvent, or, sodium nitrate and ammonium sulphate are allowed to interact in equivalent proportions, the double salt destroyed by heating (*e.g.*, to 119° C.), the solution concentrated until most of the sodium sulphate has separated, and the mother liquor, after adding more ammonium sulphate to convert the remaining sodium sulphate into double salt, is treated as above.

Hulin (Fr. P. 480150, 11th February 1915). An aqueous solution of calcium nitrate obtained, *e.g.*, by the electric arc process of fixing atmospheric nitrogen, is allowed to react with ammonium sulphate at a temperature of 120° C. or higher. The solutions are preferably raised to this temperature separately, and the preliminary heating and the reaction are effected under pressure in a series of autoclaves. The apparatus may be applied to other reactions at high temperatures under pressure, notably those producing a precipitate of calcium sulphate.

Gidden (B. P. 6048, 22nd April 1915). A suitable apparatus for the manufacture of ammonium nitrate consists of a closed vessel provided with a stirrer and thermometer, outlets at the top and bottom respectively for steam and the finished product (the latter opening being closed during the process by a plug), an inlet pipe for ammonia gas reaching nearly to the bottom of the vessel and through which hot air may also be blown if desired, and an inlet for nitric acid. Sufficient water, nitric acid, and ammonia or ammonium nitrate solution are run into the apparatus to seal the ammonia tube, and then, with the stirrer in motion, nitric acid and ammonia gas are passed in simultaneously, the rates of feed being so adjusted that the mixture is kept slightly acid. When the temperature reaches 145 to 155° C., its further increase is checked, if necessary, by the addition of water, but care must be taken that the total amount of water added, including that present in the nitric acid, does not exceed the amount which can be evaporated by the heat of the reaction. The amount of water present in the final product may be reduced to about 0.06 per cent. by blowing hot air through the charge for an hour as soon as the addition of the nitric acid and ammonia is complete, and then after the charge has been run out into trays and allowed to solidify, pulverising it in a disintegrator whilst still hot.

Ricard ((A.) Fr. P. 479164, 22nd May 1915; (B.) First addition 9th June 1915). Process of manufacturing ammonium nitrate by treating with alcohol the mother liquor from the manufacture of sodium carbonate from sodium nitrate by the ammonia process.

(A.) The mother liquor containing ammonium nitrate and sodium nitrate is evaporated to dryness or until the temperature reaches 140° C., and the residue agitated with alcohol (95 to 98 per cent.) at 70 to 80° C. Ammonium nitrate is thereby dissolved and recovered by cooling the solution and recrystallising, whilst the sodium nitrate, remaining insoluble, is returned to the ammonia soda process. The proportion of ammonium nitrate in the crude liquors or original mother liquors may be increased by adding ammonium chloride, which reacts with the sodium nitrate present to give a precipitate of sodium chloride; or ammonium sulphate may be similarly employed. Chlorides and sulphates which accumulate in the mother liquors may be removed by treating the alcoholic solution with lead nitrate. The recrystallised product contains 95 per cent. of ammonium nitrate.

(B.) The mother liquor is agitated with alcohol at 70° C. so as to precipitate sodium nitrate, leaving a solution of ammonium nitrate from which the alcohol is recovered by fractional distillation and the nitrate by crystallisation; or, the proportion of alcohol is adjusted to give an alcoholic solution of ammonium nitrate superposed upon an aqueous solution of sodium nitrate, which latter is run off and returned to the ammonia soda process.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. P. 8270, 3rd June 1915). Sodium nitrate is produced by the action of nitrous gases on sodium carbonate or bicarbonate, and is boiled with ammonium chloride solution in such concentration that sodium chloride separates and ammonium nitrate is left in solution. The sodium chloride is then treated with ammonia and carbon dioxide with the formation of sodium bicarbonate and ammonium chloride, both of which are used again for the same series of operations.

Freeth and Cocksedge (B. P. 12401, 28th August 1915). Ammonium bicarbonate is treated with sodium nitrate in solution of such concentration, that on the completion of the reaction sodium bicarbonate separates out. This is removed and washed. The liquor which is saturated with sodium bicarbonate, ammonium nitrate, and ammonium bicarbonate at the reaction temperature, is concentrated and cooled, when ammonium nitrate crystallises. This is washed with water and dried, and the washing liquor is used together with the mother liquor from the ammonium nitrate crystallisation and the washing liquor from the precipitated sodium bicarbonate for dissolving fresh quantities of sodium nitrate. For example, a reaction mixture of sodium nitrate and ammonium bicarbonate is prepared so that after the separation of sodium bicarbonate the liquor contains 161 parts by weight of ammonium nitrate, 40 parts by weight of sodium nitrate, and 100 parts by weight of water. The solution is concentrated until it contains 100 parts by weight of sodium nitrate to 122 parts by weight of water. It is then cooled to 25° C., and 40 per cent. of the ammonium nitrate originally present in the concentrated solution crystallises.

Berlin Anhaltische Maschinenbau Akt.-Ges. (Ger. P. 299602, 18th September 1915). Nitric acid is diluted with a cold saturated solution of ammonium nitrate, and during the neutralisation of the acid with ammonia gas, the solution is cooled by constantly circulating a portion through a cooler.

Ricard (Fr. P. 480082, 20th October 1915). The process is based upon the reaction between ammonium bicarbonate and sodium nitrate, and yields sodium bicarbonate and ammonium nitrate. One-third of the sodium nitrate is left undecomposed in the mother liquor, together with ammonium nitrate. The patent covers several alternative methods and apparatus for carrying out the reactions, and for separating the salts from the mother liquor. The ammonium bicarbonate and sodium nitrate may be allowed to act under pressure at 50° C. in the presence of only a small amount of water, or a saturated solution of the one salt may be allowed to act under the same conditions as regards temperature and pressure, upon the other salt in the dry state. The dried salt mixture obtained from the mother liquor is treated with hot water, which dissolves ammonium nitrate in preference to sodium nitrate, and the refined salt obtained by recrystallisation of this solution is extracted with cold water to remove sodium nitrate. The residual ammonium nitrate can be separated and dried by filtering under pressure of hot air. In order to facilitate the extraction of the raw or refined mother liquor salt by cold water, the latter is passed repeatedly through the salt by means of a pump, a jet of compressed air, or some mechanical form of agitator.

Howorth from Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. P. 101090, 24th July 1916). Solutions of ammonium nitrate act as absorbents for both ammonia and nitrous gases. One part of a dilute solution of ammonium nitrate is saturated with ammonia, and the other part with nitrous gases, and the two liquids are mixed to obtain a stronger neutral solution. The operations may be repeated at will until a concentrated solution is obtained or the solid salt separates.

Washburn (B. P. 125601, 1st September 1916). In the catalytic oxidation of ammonia, the stream of ammonia and air is passed through the apparatus at such a rate that some of the ammonia escapes oxidation, so that a mixture of NH_4NO_3 and HNO_3 is obtained. A suitable apparatus is specified.

Tyrer (B. P. 125621, 19th September 1916). Two molecular proportions of sodium nitrate and one of ammonium sulphate are dissolved in as little water as possible, and the filtered solution is concentrated until it boils at about 120° C. The liquor is filtered hot, 60 to 70 per cent. the theoretical amount of sodium sulphate remaining on the filter, and then a little water and sufficient calcium nitrate solution to precipitate about 60 per cent. of the remaining sulphate are added to the filtrate. After removal of the calcium sulphate the liquor is concentrated until it boils at 120° to 125° C., allowed to cool, and the ammonium nitrate which crystallises out is separated by filtration, washed and dried. The diluted mother liquor is used for dissolving fresh quantities of sodium nitrate and ammonium sulphate, and the process is repeated.

Nauckhoff, Nitroglycerin Aktieb (Swed. P. 41936, 31st January 1917). Liquid HNO_3 and NH_3 in solution or as a gas are conducted separately into a closed mixing vessel, provided with inlet and outlet. The mixture is conducted in a continuous stream, while cooling, and brought into contact with the walls of the apparatus.

Freeth and Cocksedge (B. P. 126678, 7th February 1917; U.S. P. 1301047, 15th April 1919). Ammonium nitrate is obtained by precipitating a solution saturated with ammonium nitrate, sodium nitrate, and sodium sulphate at a selected temperature, adding enough water to keep the sodium salts in solution at a selected lower temperature, and then cooling the diluted solution to that temperature when ammonium nitrate separates out. The mother liquor is then concentrated until the added water has been removed, and quantities of ammonium sulphate and sodium nitrate equivalent to the separated ammonium nitrate are then added, the whole being maintained at a temperature not lower than the original selected temperature. Na_2SO_4 separates and is removed, and the whole series of operations can then be repeated indefinitely.[1]

Washburn (U.S. P. 1217247, 27th February 1917). A mixture of gases containing ammonia and oxygen is subjected to the action of a catalyst at such a rate that the reaction product contains nitrous gases, and not more than 20 per cent. of free ammonia. A solution of nitric acid and ammonium nitrate is produced from the reaction product, and free ammonia is added to convert all the nitric acid into nitrate, which may be isolated and treated to yield concentrated nitric acid.

Blom (Can. P. 178884, 21st August 1917). Ammonium nitrate solutions are saturated with ammonia and then neutralised with nitric acid. Saturation and neutralisation are repeated until the ammonium nitrate separates and the mother liquor is used for re saturation.

Washburn (U.S. P. 1206062, 28th November 1917). The reaction of oxidation of ammonia is carried on at such a rate that not more than 20 per cent. free ammonia and nitrous gases are present in the reaction products. A solution of nitric acid and ammonium nitrate is formed from these gases, concentrated and neutralised with ammonia if ammonium nitrate is the product desired, or treated with sulphuric acid to recover nitric acid and ammonium sulphate.

Partington, Graham, and Jones (B. P. 134562, 1st February 1918; U.S. P. 1306924, 17th July 1919). Ammonium nitrate produced in the form of a mist by the interaction of ammonia gas and nitric acid, or by other means, is caused to pass through a dehydrating agent, such as

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[1] *Cf.* B. P. 16454, of 1910.

sulphuric acid, and can then be readily condensed and collected. Very little mist is absorbed by the sulphuric acid.

Blom and Norsk Hydro-Elektrisk Kvaelstofaktieselskab (U.S. P. 1256513, 19th February 1918). An ammonium nitrate solution is saturated with ammonia and then neutralised with nitric acid liquor obtained by absorbing nitrous gases in ammonium nitrate solution. A portion of the neutralised liquor is treated with ammonia and another portion with nitrous gases, and these steps are successively continued to form ammonium nitrate. This method avoids overheating and formation of large amounts of fumes.

Partington, Jones, and Brownson (B. P. 136190, 4th March 1918; U.S. P. 1330136, 10th February 1920). Ammonium nitrate is manufactured by bringing together oxides of nitrogen, oxygen, water, and ammonia in such proportions that the oxygen is in excess of the theoretical quantity required to convert the oxides of nitrogen into nitrogen peroxide, the ammonia is insufficient to react with the whole of the oxides of nitrogen, and the water does not exceed the amount necessary to convert all the ammonia into ammonium nitrate by interaction with the oxides of nitrogen. Where gases containing about 10 per cent. of oxides of nitrogen are utilised, the amount of oxygen should be approximately three to four times the theoretical quantity, and time should be allowed for the reaction to take place before the admixture with the ammonia. If the gases after any stage of the process still contain oxides of nitrogen, a further quantity of oxygen, ammonia, and water may be added to produce more ammonium nitrate. By this process less ammonium nitrate is lost than by other methods of manufacture.

Bailey, Denny, and Jeffries (B. P. 131017, 20th March 1918). Suitable proportions of ammonium sulphate and sodium nitrate interact in the presence of a bisulphate, *e.g.*, $NaHSO_4$. Na_2SO_4 separates from the hot solution and is removed. When the solution has cooled, without dilution, ammonium nitrate and not the double salt separates. Ammonium sulphate and sodium nitrate in proper quantities are added to the final solution, and the process is made continuous. Nitre cake may be used as the source of the $NaHSO_4$ employed.

Rivett (B. P. 131358, 16th May 1918). Ammonium nitrate is produced by bringing together ammonium sulphate and sodium nitrate in the presence of water at, say, 55° to 65° C., filtering off the precipitated sodium sulphate, passing in gaseous ammonia to effect a further separation of sodium sulphate as such or as a double salt $NH_4 . Na . SO_4$, removing the ammonia from the solution by heat or reduced pressure, or both, and then cooling to effect the separation of the NH_4NO_3.

The mother liquor after separation of the ammonium nitrate, with or without the addition of the salts precipitated by the ammonia treatment, may be used to dissolve more ammonium sulphate and sodium nitrate.

Carlson (Swed. P. 44650, 23rd October 1918). Ammonia is introduced into several vessels in series, provided with coolers, then nitric acid is run into the first vessel and the resulting liquor is passed through the series so that reaction occurs in several subdivisions to maintain the temperature and increase production.

Freeth and Cocksedge (B. P. 149095, 20th May 1919). Ammonium sulphate and sodium nitrate are caused to react in suitable proportions, and the sodium sulphate precipitated is removed. Calcium sulphate is added to the solution to separate sodium sulphate as a double salt. After removal of this salt, ammonium nitrate may be obtained by cooling the solution without further dilution, the mother liquor being used for a fresh cycle of operations.

Uhde (Can. P. 201894, 13th July 1920). Ammonium nitrate is produced from coal distillation gases by separating the tar but not the water vapour from the gases while still hot, conducting the gases into an alkaline earth nitrate solution at 100° C., filtering the solution and evaporating to produce the salt.

Landis (U.S. P. 1315674, 9th September 1919). Ammonia is passed into a solution of nitric acid to neutralise the solution and form ammonium nitrate, and the vapours which are produced in the reaction are recovered and returned to the solution by the action of a reflux condenser.

Treatment of Ammonium Nitrate.

Gallup, for du Pont de Nemours (U.S. P. 1131361, 9th March 1915). Ammonium nitrate solution is concentrated to a degree depending on the size of grain required, and the salt is then crystallised by cooling, whilst stirring and aerating the solution.

(*a*) Ger. P. 305567, 31st January 1917; (*b*) Ger. P. 305568, 8th January 1918. (*a*) Ammonium nitrate (melting-point 152° C.) is mixed with di-cyano-diamide (melting-point 205° C.), a mixture containing 85 per cent. of the former becoming fluid at 115° C. The use of the mixture in the preparation of explosives is easier and less dangerous than that of ammonium nitrate alone. (*b*) Water is used as the liquefying medium. The pouring temperature of a mixture of 66 per cent. ammonium nitrate, 10 per cent. sodium nitrate, 20 per cent. nitrotoluol, and 4 per cent. water is about 80° C.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. P. 117823, 10th April 1917; Fr. P. 485107, 13th December 1917). Ammonium nitrate is obtained in dry granular form suitable for agricultural purposes by drying a moist mixture of ammonium nitrate with bog iron ore or kieselguhr at a temperature not above 130° C. with agitation. A small quantity of plaster of Paris (gypsum) may be added to the ammonium nitrate before treatment, and the suspension of bog iron ore which is preferably employed can be rendered more viscous by adding gelatinised starch, kieselguhr, potassium salts, or ammonium salts. The drying may be effected in two stages, first at a comparatively low temperature such as 20° to 40° C., and then at a higher temperature such as 100° C.

Gallup (Can. P. 179253, 11th September 1917). The ammonium nitrate liquor is concentrated to a predetermined concentration according to the size of grain required, and is allowed to crystallise while being stirred and aerated on cooling. If the liquor has a relatively high temperature of crystallisation, the grains of ammonium nitrate will be relatively large, and vice versâ.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Swiss P. 76202, 16th November 1917). Ground ammonium nitrate is mixed with a binder which is not adhesive when dry, with the addition of water, and the mixture is dried with stirring for the purpose of forming larger grains from the original small crystals. A colloidal substance serves as the binder. The drying may be effected with gradual rise of temperature. Dehydrating may be applied to the ammonium nitrate before mixture with the binder. The dried product may, with advantage, be subjected to the action of a vacuum.

Bergve and Landby (U.S. P. 1263363, 23rd April 1918). Ammonium nitrate is mixed with about 3 per cent. of plaster of Paris, the mixture is moistened and dried while agitated at a temperature of 90° to 110° C. to produce a product which is granular and suitable for use in fertilisers.

Bergve (Can. P. 182916, 12th March 1918). Solid ammonium nitrate is moistened with a liquid containing an inorganic substance (bog iron ore which with water produced a viscous liquid), is dried, then heated while being agitated.

Hinselmann (Ger. P. 284641) obtains ammonium nitrate (or chloride), remaining white on keeping in stock, and free from sulphocyanide, by heating below the temperature of volatilisation, whereby the sulphocyanide is converted into a black powder (persulphocyanide), from which the pure solution of nitrate (or chloride) can be separated by filtration. In the case of ammonium nitrate, the heating must be carried on at 135° to 140°, in that of ammonium chloride at 200° to 250°.

Gallup and the Du Pont de Nemours Powder Company (U.S. P. 1131361) evaporate the solution of ammonium nitrate in two superposed pans. If the temperature of the top pan is kept at 135° to 138°, the product obtained in the bottom pan is in a granular form. With a temperature of 150° in the top pan, the product comes out in a much coarser form, of which no more than 5 per cent. passes through a ten-mesh sieve. The grains are nearly globular and comparatively very little hygroscopic.

Manufacture of Calcium Nitrate.

Braunschild and Chapiro (Fr. P. 428014, 11th June 1910). Sodium nitrate solution is treated with ammonium carbonate (or ammonia) and carbonic acid, or with ammonium bicarbonate so as to produce ammonium nitrate solution and a deposit of sodium bicarbonate, and the ammonium nitrate is treated with lime or calcium carbonate, thus forming calcium nitrate solution which is concentrated, and ammonia, or ammonium carbonate, which is used again. In the first part of the process some sodium nitrate remains undecomposed, and this may either be removed by crystallisation, before the treatment with lime, or be allowed to remain, so as to give finally a mixture of sodium and calcium nitrates, which is used as a manure. Claim is also made for a product containing in addition, ammonium phosphate or sulphate produced by neutralising any ammonia not driven off.

Soc. Norvegiénne de l'Azote et de Forces Hydro Electriques (Fr. P. 442514, 21st June 1911). Commercial calcium nitrate (such as that employed as a fertiliser) is heated for a relatively short time, in a rotating cylinder or in other manner, to a temperature slightly above its fusion point, so that the finer particles melt more or less completely and the coarser particles remain unmelted or are fused superficially only, thus giving, by agglomeration, a granular product. By mixing other finely divided substances, such as calcium cyanamide, with the nitrate, these may be incorporated in the granules.

Peacock and Southern Electro Chemical Company (U.S. P. 1057876, 1st April 1913). Phosphate rock containing tricalcium phosphate and free lime is finely powdered and immersed in water; gases containing nitric acid are blown through the mixture until all the free lime and one-third of the calcium contained in the tricalcium phosphate are converted into calcium nitrate, the latter solution being then separated from the dicalcium phosphate which has been formed.

T. Twynam (B. P. 5784, 28th February 1914). Finely ground basic phosphatic slag is heated with restricted amount of nitric acid insufficient to act upon the compounds or form any notable quantity of gelatinous silica, nitric acid preferably being obtained from air by electric arc process. After drying the deliquescent mass obtained may be converted into dry condition by adding potassium soda sulphate. Calcium nitrate may be separated by solution.

T. Twynam, E. K. Scott, and F. Howles (B. P. 6275, 12th March 1914). Phosphatic basic slags are subjected to action of oxides of nitrogen and air issuing from nitrogen fixation furnace in which oxides are produced by high tension electric arc, whereby slag gives rise to substances containing soluble phosphate and nitrates of bases present in slag. Temperature of mass is controlled to prevent formation of nitrate of iron by injecting water, steam, or sludge of ground slag and water.

Smith and Ammonia Soda Company (B. Ps. 10595, 21st July 1915, and 1059, 22nd January 1916). In the manufacture of calcium nitrate by the reaction of calcium chloride on sodium nitrate in solution, the calcium chloride is employed in excess, *e.g.*, an excess of 20 per cent. and the mixed solution is evaporated, *e.g.*, until its boiling-point is 130° to 140° C., and then cooled or allowed to cool, *e.g.*, to 60 C., the sodium chloride which separates during these operations being removed; then the solution is diluted, *e.g.*, until its boiling-point would be about 128° C., and is then further cooled, whereupon calcium nitrate crystallises out and is washed with water or calcium nitrate solution, and if desired may be recrystallised. In recrystallising, a solution of a boiling-point of about 121° C. may be employed, and the mother liquor may be used for washing the crystals first obtained or for diluting the original solution prior to the first crystallisation.

Gillbert (B. P. 124780, 27th March 1916). Calcium nitrate is obtained by the addition of equivalent quantities of calcium chloride and sodium nitrate to a "nucleus solution," in such quantities as to produce a solution saturated with calcium nitrate at as high a temperature as practicable, say 80° C., and the precipitated sodium chloride is removed. Water is then added in quantity sufficient to make the proportion of water to sodium chloride equal to that of the nucleus solution, and to provide four molecules of water of crystallisation for the calcium nitrate which is to be separated. The solution is then cooled to a predetermined temperature to separate the calcium nitrate, leaving the nucleus solution, which is used again, and so on indefinitely, the subsequent cycles, however, including a step of evaporating, before the separation of sodium chloride, a quantity of water equal to that which was added in the first cycle. The nucleus solution is a solution saturated with calcium nitrate, sodium nitrate, and sodium chloride, if the separation of calcium nitrate is to be effected below 25° C., or a solution saturated with calcium nitrate and sodium chloride if the separation of calcium nitrate is to be effected above 30° C. in practicable quantities.

Thorssell (Can. P. 189603, 15th April 1916). A solution of calcium cyanamide is mixed with a solution of calcium nitrate and brought into intimate contact with nitrifying bacteria during ample supply of air. A small part of the calcium nitrate already formed is set aside for preparing the finished product, and the rest is mixed with fresh calcium cyanamide solution and used for obtaining a stronger nitrate solution.

H. G. F. Gould-Adams, J. R. Partington, and E. K. Rideal (B. P. 129699, 29th November 1917). Oxides of nitrogen such as are produced, for instance, in electric arc process or ammonia oxidation processes are allowed to react with any suitable oxide or carbonate in solution or suspension, and the nitrite which is first produced along with nitrate is oxidised to nitrate by further treatment with the nitrogen oxides; lower oxides of nitrogen resulting from the second reaction are mixed with fresh supply of air or oxygen and used for treatment of more liquor. Process may be carried out in an alternating series of absorption and oxidation chambers on counter-current principle, or each absorption chamber may be capable of isolation for purposes of emptying and re-charging.

Blumenberg (U.S. P. 1259717, 19th March 1918). Calcareous borax ore is treated with nitric acid to form H_3BO_3 and $Ca(NO_3)_2$, the mixture is evaporated to dryness to render the silicates insoluble, the mass is digested with boiling water, H_3BO_3 is separated from the $Ca(NO_3)_2$ by crystallisation after filtering, H_3BO_3 and $NaNO_3$ are mixed in proportion to form borax, and this mixture is heated under less than atmospheric pressure in the presence of oxygen and water vapour, the HNO_3 given off being used for treating additional ore. U.S. P. 1259718 relates to a similar method in which the $Ca(NO_3)_2$ is heated in a closed vessel with oxygen and water vapour to form HNO_3 and CaO.

U.S. P. 1259719 specified heating calcareous borax ore with $NaNO_3$ to form a fused mass which is digested with water. The sodium borate is separated from the calcium nitrate in the solution obtained by cooling and crystallisation.

Thorssell and Lunden (B. P. 131493, 26th September 1918).

Calcium nitrate is formed by bacterial oxidation of calcium cyanamide by trickling a solution of the latter over a bacterial bed formed, *e.g.*, by a layer of garden soil mixed with powdered coke. Calcium cyanamide is dissolved in water which may contain CO_2 to precipitate free lime, and sufficient of the solution is added to a solution of calcium nitrate to obtain complete oxidation of the cyanamide in one treatment. Part of the calcium nitrate is separated, and to the remainder, cyanamide solution is added to obtain a solution of the same composition as that previously treated.

Thorssell and Lunden (U.S. P. 1286839, 3rd December 1918). Calcium cyanamide is dissolved in water and mixed with a solution of calcium nitrate, and the mixture is then treated with nitrifying bacteria and air to effect further production of calcium nitrate.

Nitrum Akt.-Ges. (B. P. 130979, 28th July 1919). A concentrated solution of calcium nitrate is obtained from nitrous gases, by neutralising with lime the acid solution obtained by dissolving the gases, and using the neutralised solution for further absorption. The neutralisation may be effected by passing the solution over limestone in the absorption apparatus, or by adding lime or limestone to the solution outside the absorption apparatus, the neutralised solution being returned thereto.

Treatment of Calcium Nitrate.

Brougham and Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Fr. P. 445286, 11th July 1911; B. P. 15934, 8th July 1912). The concentrated solution of calcium nitrate is strongly cooled and agitated, with the formation of a mass of solid particles suspended in the saturated fluid, and the viscous mixture is run in a thin layer over the surface of a cooled rotating drum, provided with a scraper, whereby solid calcium nitrate is continuously removed in the form of fine flakes.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Fr. P. 466963, 3rd January 1914; B. P. 468, 7th January 1914). The molten substance is formed into globules and allowed to fall freely in a gaseous atmosphere, such as air, which may be circulated in the opposite direction and submitted to cooling. Powdered material may be added to the melt immediately before granulating.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Fr. P. 474996, 11th July 1914). Material which has been allowed to solidify or dry on a drum is removed by a scraper and immediately reduced to a granular powder by contact with a strip of wood or metal, which may be adjusted at the desired distance from the drum and scraper, and at a suitable angle. A current of air or other gas is employed, when necessary, to prevent the particles from adhering to each other as they are produced.

Hechenbleikner for Southern Electro Chemical Company (U.S. P. 1143625, 22nd June 1915; Can. P. 191308, 1st July 1916). "Fluid nitrate of lime" is collected into pools, around which a cooling medium is circulated. The cakes so formed are detached from the moulds by heating the walls, and then pulverised and conveyed away in a current of air.

Holter (U.S. 1203740, 7th November 1917). Granular calcium nitrate is made without formation of powder by melting the material and, when it is in sufficiently concentrated form for crystallisation, forming it into drops or globules and hardening them by a counter-current of air through which they pass.

Manufacture of Barium and Strontium Nitrates.

K. Puls, K. Krug, and Norddeutsche. chem. Fabr. (Ger. P. 198861, 11th August 1907). Finely powdered barium carbonate (witherite) or strontium carbonate (strontianite) is heated with an aqueous solution of calcium nitrate under steam pressure and with agitation, the calcium carbonate produced is filtered off, and the solution of barium or strontium nitrate is evaporated.

Traine and Hellmers (Ger. P. 205167, 3rd January 1908). Barium and strontium nitrates are prepared by heating the corresponding sulphides or hydrosulphides with calcium nitrate, preferably under pressure.

H. Weyer (B. P. 9773, 5th May 1908). Barium or strontium sulphide obtained by heating the corresponding sulphate to incandescence with coal, is treated with molten calcium nitrate, or with a heated solution of the latter in water, preferably under pressure. Barium or strontium nitrate goes into solution, while sulphur, calcium sulphide, and calcium hydrosulphide are deposited. Carbon dioxide is then passed into the heated liquid, and the escaping hydrogen sulphide "treated to form sulphur, sulphurous acid, or sulphuric acid." After filtering, the solution is evaporated to recover pure barium or strontium nitrate.

H. Weyer (B. P. 9772, 5th May 1908). Calcium nitrate in solution undergoes double decomposition with the hydroxide, oxalate, or phosphate of barium or strontium, when heated, in soluble calcium compounds and a solution of barium or strontium nitrate being formed. The reaction is best effected under pressure.

Chem. Werke vorm Dr H. Byk (Ger. P. 242243, 31st December 1909). Barium carbonate is fused with calcium nitrate. If commercial barium carbonate containing sulphide be used, the fusion is prolonged until H_2S is no longer evolved. The further treatment of the product follows according to known methods. The process possesses the advantage over the one described in Ger. P. 205167 of 1908, that the fusion may be effected in open vessels.

Akt.-Ges. für Chemische Industrie and Kühne (Ger. P. 248524, 26th November 1911). Barium sulphate (1 molecule) is fused with an excess (2 molecules) of calcium nitrate, the fused mass is suddenly cooled and lixiviated with water to extract the barium nitrate formed. Up to 75 per cent. of the barium sulphate is converted into nitrate.

Snelling (U.S. P. 1285824, 26th November 1918). Barium nitrate is prepared by spraying nitric acid into a solution containing barium sulphide, spreading the mixture into thin sheets and maintaining sub-atmospheric pressure above the liquid to remove the H_2S as fast as formed. Other nitrates such as strontium nitrate may be similarly prepared from the corresponding sulphides. Removal of H_2S avoids reduction of HNO_3 and consequent formation of ammonium nitrate.

Davis (U.S. P. 1321013, 4th November 1919). Barium nitrate is made by mixing saturated solutions of barium sulphide and aluminium nitrate at a temperature of 50° C., and then preferably raising the temperature of the reacting materials to 100° to 120° C., at which temperature the solution boils and the reaction is vigorous. H_2S produced in the process may be carried out continuously. Aluminium hydroxide is obtained as a precipitate. Other alkaline earth nitrates may be similarly produced.

Manufacture of Copper Nitrate.

Gouthière et Cie and Ducancel (Fr. P. 395806, 7th January 1908). A solution of copper nitrate for use in agriculture and viticulture is made by mixing solutions of commercial calcium nitrate and copper sulphate. The product is claimed to be most active if prepared just before use.

Manufacture of Aluminium Nitrate.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. P. 120035, 23rd July 1918). Aluminium nitrate is prepared from clay, argillite, etc., by heating the mineral with nitric acid, in an autoclave under pressure, whereby dissociation of the nitric acid at high temperatures is prevented. The silica which separates is in a granular state and is easily removed by filtration.

Manufacture of Lead Nitrate.

Anderson and Kaar (U.S. Ps. 1083910 and 1083911, 13th January 1914). Crude lead sulphide is digested with dilute nitric acid (7 per cent. strength) containing an alkali nitrate, and the solution purified by the addition of successive small quantities of an alkali. Iron is eliminated from the solution by first heating the latter with sufficient sodium carbonate to precipitate the greater part of this impurity, and then with that necessary to precipitate the remainder.

Manufacture of Nitrates (General).

Eyde (B. P. 28614, 28th December 1904). To the solution of mixed nitrates and nitrites produced by the action of nitrous gases on alkali or alkaline earth hydroxides or carbonates, nitric acid is added, and the nitrous vapours evolved are utilised, preferably by returning them to the apparatus in which the mixture of such nitrates and nitrites is produced. The nitric acid in adequate proportion may be added to the boiling, or to the cold solution of the mixture; but in the latter case a current of air is passed through the solution.

Brünler and Kettler (Fr. P. 380467, 2nd August 1907). A mixture of combustible gas and air or oxygen is burnt under water (or alkali solution) in such a manner that the flame issues into the liquid. The quantity of nitrogen is so regulated that the temperature of the flame lies, in its interior, within the limits of stability of nitric oxide, and in its exterior portion, within the limits of stability of nitrogen peroxide. Under these conditions nitric oxide is formed in the hot interior of the flame, and in the cooler mantle combines with oxygen to give nitrogen peroxide, which in the presence of water and oxygen is converted into nitric acid (or alkali nitrate). Burning the mixture under increased pressure is found to improve the yield.

Badische Anilin und Soda Fabrik (Ger. P. 210167, 11th July 1908).

Johnson and Badische Anilin und Soda Fabrik (B. P. 10867, 7th May 1909). The object of the invention is to prepare technically pure solid nitrates from gaseous mixtures containing small proportions of oxides of nitrogen such as are obtained, for instance, by the electrical oxidation of atmospheric nitrogen. The gases are mixed with steam or with atomised water, the mixture being kept at a temperature above the boiling-point of nitric acid, and then brought in contact with solid oxides, hydroxides, or carbonates of the alkalis or alkaline earths. At the temperature employed (*e.g.*, 250° C.), after the addition of the water, a large portion of the nitric acid is in the dissociated condition, but when the mixture is brought in contact with the absorbent, the undissociated nitric acid is immediately absorbed, after which further quantities are produced from the dissociation products and absorbed, and so on until the whole of the nitric acid is absorbed.

Dyes and Lehmann (B. P. 15391, 21st July 1908). Calcium nitrate is treated with a very slight excess of ammonium sulphate in aqueous solution, whereby practically all the calcium sulphate formed is precipitated, and after filtering, the clear solution of ammonium nitrate is evaporated. If the ammonium nitrate is required quite free from sulphate, its solution is first treated with the amount of barium nitrate, or baryta water, which is equivalent to the excess of ammonium sulphate present, after which it is filtered and evaporated.

Kettler (Fr. P. 396161, 11th November 1908). The apparatus consists of a furnace which is heated by the combustion of a mixture of gas and air passing through it, and contains a spiral of refractory metal or porcelain, through which passes a mixture of nitrogen and oxygen. The temperature of the mixture is thus brought to 1300° to 1400° C. The front part of the spiral is further heated by being enclosed in a tube, in which a mixture of benzene or other inflammable vapour and oxygen is burned, and the temperature of the gas is thus raised to about 2000° C. A further increase to 2400° to 2600° C. is effected by injecting a mixture of acetylene and oxygen into the flame issuing from the spiral, or an electric arc may be disposed in front of the nozzle. The flame which now contains nitric oxide enters a sheet-iron pipe of comparatively large rectangular section, slightly inclined in the direction of the flame, and enclosed in a vessel filled with a solution of lime or other base, which completely surrounds the pipe. In this pipe peroxidation takes place, and, when desired, the solution can be introduced as a shower through a grating arranged in the upper surface of the pipe, thus suddenly cooling the flame and absorbing the oxide with formation of nitrate, the solution being pumped back into the vessel until neutralised. A special opening is provided for observing the flame as it leaves the spiral.

Badische Anilin und Soda Fabrik (Fr. P. 398738, 23rd January 1909). Alkaline earth nitrites or mixtures containing them, such as those obtained by using alkaline earth bases as absorbents of nitrous gases, are treated at about 300° C. with the higher oxides of nitrogen, preferably in the presence of air or oxygen; they are thus completely converted into nitrates, and nitric oxide is also produced, which acts as a carrier of oxygen to a further quantity of nitrite.

Badische Anilin und Soda Fabrik (Ger. P. 220539, 16th February

1909; U.S. P. 1039325, 24th September 1912). Nitrites or mixtures of nitrites and nitrates such as are obtained in processes for the utilisation of atmospheric nitrogen, are treated with nitric acid, and the nitrous vapours produced are mixed with such a quantity of oxygen, or a gaseous mixture containing oxygen, that the atomic ratio of the total oxygen to the combined nitrogen is as nearly as possible 5 : 2. The gases can then be absorbed in water (or aqueous solutions) in a relatively small absorption apparatus, yielding concentrated nitric acid. In using the process in connection with the manufacture of nitric acid and nitrates from atmospheric nitrogen, the oxygen is added in the form of the gaseous mixture obtained by the combustion of atmospheric nitrogen, and the solution of nitrite and nitrate obtained in a later stage of such manufacture is used for the absorption of a part of the nitric acid, and is then added to another portion of the nitrite-nitrate mixture in order to convert it wholly into nitrate.

P. A. Guye and G. Darier (Fr. P. 415143, 5th July 1909; U.S. Ps. 1036611 and 1036833, 27th August 1912; Ger. P. 242014, 3rd July 1910). The process consists in allowing nitric acid, of less than 35 per cent. strength, to react with an alkali or alkaline-earth chloride, at a temperature below 80° C., and under a pressure below 300 mm., the dilution being maintained, as far as possible, during the operation. A current of air may be passed through the apparatus, instead of working under reduced pressure, and in order to convert any oxides of nitrogen present in the gases into nitrates, these gases mixed with air or oxygen if desired, are passed through apparatus filled with solid chloride, before the hydrochloric acid is recovered by solution in water. With sodium chloride, for instance, working at 22 mm., about 93 per cent. of the nitric acid used may be transformed into nitrate in the reaction vessel, the remainder being almost entirely retained as nitrate by the solid chloride.

Badische Anilin und Soda Fabrik (Ger. P. 223026, 31st July 1909, addition to Ger. P. 220539, 16th February 1909). According to the chief patent nitrites or mixtures of nitrites and nitrates were converted into nitrates by treatment with nitric acid, the nitrous fumes evolved being mixed with oxygen or a gaseous mixture containing oxygen and then absorbed. In the process it is necessary that the solution be kept slightly acid, and in order that this may be effected even when the proportion of nitrite is variable, it is proposed, according to the present patent, to mix the nitric acid recovered by absorption from the nitrous fumes with a small excess of nitric acid, and use it for the treatment of a further quantity of the mixture containing nitrite or nitrite and nitrate. In this way the process may be worked continuously, the supply of nitric acid being regulated essentially by the nitrite content of the mixture.

Badische Anilin und Soda Fabrik (Fr. P. 411674, 18th January 1910); Johnson (B. P. 30502, 30th December 1909). Aqueous solutions of nitrites, or of mixed nitrites and nitrates, are submitted to the action of nitrous gases or of gaseous mixtures containing such. Or, they are treated with nitric acid, and the nitrous gases evolved are mixed with a slight excess of oxygen or gas containing oxygen, such as nitrous gases from an electric furnace for the combustion of air, and are absorbed by water or an aqueous solution, to give nitric acid again, and, since relatively strong acid may be obtained in this way, the process may be utilised for the concentration of dilute nitric acid. To avoid making very dilute nitrate solutions, the nitrite may be decomposed by a solution of nitric acid containing nitrate, the evolved nitrous gases, after mixing with oxygen, being absorbed, for instance, by the liquor itself in a suitable tower. In order to prevent waste of acid in the continuous production of nitrate, if the strength of the nitrite solution should vary, the nitric acid obtained by absorption may be at once mixed with fresh nitrite solution and a slight excess of nitric acid, so that the admission of acid is regulated by the concentration of the nitrite solution. If impurities such as carbon dioxide be present in the gases evolved by the action of acid on the nitrite, they are absorbed by alkali before the gases are mixed with oxygen. Free nitrous acid is eliminated from solution of nitrates, or other liquids containing it by treating them with air or other gas, or by reduction of pressure, or by atomisation of the liquid.

Pauling (B. P. 9884, 22nd April 1910); Salpetersäure Ind.-Ges. (Fr. P. 415749, 9th May 1910); Pauling (U.S. P. 1991356, 2nd May 1911). The process consists in causing a current of air containing oxides of nitrogen to meet an opposing stream of alkali (*e.g.* in a series of towers); some of the resulting nitrite is, however, separated by evaporation of the lye at a given point (after it has traversed some of the towers, for instance), and nitrate is crystallised from the residual liquor (containing approximately equal proportions of nitrate and nitrite) after it has passed through the rest of the system, when nitric acid is mainly absorbed and nitrite is decomposed with the formation of nitrate.

Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Fr. P. 425997, 13th February 1911; U.S. P. 1110481, 15th September 1914). A mixture of a nitrite and a nitrate is treated with a quantity of nitric acid equivalent to the amount of nitrite present, and the nitrous gases, which are evolved, are absorbed with restricted access of air by an alkaline solution, with the formation of pure nitrite; the residue of the mixture treated consists of pure nitrate.

Hampel (Ger. P. 321030, 11th March 1919). The acid radical of the initial salt is precipitated in a slightly soluble form, and then converted into a soluble salt in combination with a less soluble one by the action of ammonia and an acid gas or anhydride. These salts in turn are treated with the desired acid for the end product, in its free state, by which means the initial precipitating salt for the process is recovered. The method is applicable to the production of nitrates of potassium, sodium, and magnesium, the sulphates being first treated with calcium nitrate, the precipitated calcium sulphate then converted into calcium carbonate and ammonium sulphate by means of ammonia and carbon dioxide, and the calcium carbonate finally converted into calcium nitrate by treatment with nitric acid.

Hood (B. P. 149783, 20th May 1919). Normal aluminium nitrate is prepared by double decomposition of aluminium sulphate with calcium, barium, or potassium nitrate.

CHAPTER VIII

AN ACID AND WATER BALANCE

Contractions Used.

T.N.A. = Total Nitrogen Acids (expressed as HNO_3).
S.A. = Sulphuric Acid.
N.A. = Nitric Acid.
S.N.A. = Strong Nitric Acid.
W.N.A. = Weak Nitric Acid.
R.V.A. = Revivifying Acid.
M.A. = Mixed Acid.
N.Co. = Nitro-Cotton.
N.G. = Nitro-Glycerine.

INTRODUCTION.

In order to manage an acids factory successfully, where there is a circulating system, it is essential to know—

(*a*) The effect any particular programme of work will have on the stock of acid at each plant;
(*b*) The most economical method of dealing with the acids involved.

Without a knowledge of (*a*) the working would be chaotic and might lead to stoppages owing to some storage systems becoming too full and others too low. Unless (*b*) is investigated the vital question of cost is neglected.

The case considered here is that of an acids factory which has to deliver nitric acid in suitable form for the production of nitro-glycerine and nitro-cotton. The following equations serve to illustrate the formation of these important nitrates:—

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(O\,.\,NO_2)_3 + 3H_2O$$

Glycerine + Nitric Acid = Nitro-Glycerine + Water

$$(C_6H_{10}O_5)_2 + 6HNO_3 = C_{12}H_{14}(NO_3)_6O_4 + 6H_2O$$

Cellulose + Nitric Acid = a Nitro-Cellulose + Water

In actual practice the NO_3 radical is supplied as nitric acid, and this is mixed with sulphuric acid, since the formation of the nitrates takes place much better in its presence.

NITRIC ACID CONSUMPTION.

In the nitration processes, nitric acid is consumed and water is produced. To keep the nitric acid content of the system constant, it is necessary to introduce a corresponding amount of fresh nitric acid. Further, in actual practice, each plant handling nitric acid has a certain working loss and this amount increases the consumption figure.

The fresh nitric acid is introduced into the system by the nitric acid retorts which manufacture nitric acid from nitrate of soda and sulphuric acid. The NO_3 radical is thus introduced to the acid system in the form of nitrate of soda.

WATER.

The spent acids returned from the nitrating plants contain the water introduced by the chemical reactions and in the process of washing the nitrated cotton and glycerine. Water is also introduced to the system in various other ways, *e.g.*, in absorption towers, denitrators, etc.

For the preservation of a balance in the acid system, all added water must be removed. This is done at the sulphuric acid concentration plant, and at the oleum plant where manufactured SO_3 absorbs water from the system.

SULPHURIC ACID CONSUMPTION.

Theoretically there should not be consumption of sulphuric acid at any part of the acids section except the nitric acid retorts. Here it is used for the decomposition of nitrate of soda.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

This usage represents total loss of sulphuric acid to the section. In practice, all plants handling sulphuric acid lose a little, and this amount must be reckoned as consumption.

Sulphuric acid is in this instance re-introduced to the system by the Grillo oleum plant which manufactures oleum, using sulphur as the raw material.

REQUIREMENTS FROM VARIOUS PLANTS.

Grillo Oleum Plant.

To produce oleum (104·5 per cent. H_2SO_4). The SO_3 produced is absorbed by "feed acid" (93 per cent. H_2SO_4).

Nitric Acid Retorts.

To produce nitric acid. The acid is produced as strong nitric acid (S.N.A) and as weak nitric acid (W.N.A), a portion of the W.N.A coming from the absorption system of the plant.

Stills.

To separate the nitric and sulphuric acids from (*a*) spent acid (from the nitration of cotton); (*b*) specially mixed acid.

In the process both S.N.A and W.N.A are produced. In addition, weak sulphuric acid (78 per cent. H_2SO_4) is produced.

Denitration.

To separate and recover the nitric and sulphuric acids in spent acid from the nitration of glycerine. Owing to the use of steam for denitration purposes the acids produced are relatively weak.

Sulphuric Acid Concentrators.

To concentrate all the weak sulphuric acid produced. Water is expelled from the system as steam.

Mixing.

To mix acids as required. It may also conveniently control stocks of and deliver the concentrated sulphuric acid of the acid section.

PREPARATION OF BALANCE FOR PRODUCTION OF 100 TONS OF CORDITE. (See Fig. 132.)

The necessary data are the results of actual working experience on the various plants as shown on flow sheets for previous periods.

Naturally, as experience grows, the more nearly is one able to forecast actual plant efficiencies and recoveries, and the balance becomes more and more delicately adjusted.

Data.

The following figures are drawn from considerable working experience :—

Nitro-glycerine required	43 tons
Nitro-cotton required	53 tons
Mixed acid required per ton of nitro-glycerine	2·658 tons
Composition—	
H_2SO_4 58·5 per cent. ; T.N.A. 40·4 per cent. ; H_2O 1·1 per cent.	
Spent acid produced per ton of nitro-glycerine	2·004 tons
Composition—	
H_2SO_4 74·3 per cent. ; T.N.A. 8·7 per cent. ; H_2O 17·0 per cent.	
Mixed acid required per ton of nitro-cotton	20·092 tons
Composition—	
H_2SO_4 62·15 per cent. ; T.N.A. 23·00 per cent. ; H_2O 14·85 per cent.	
Spent acid produced per ton of nitro-cotton	20·077 tons
Composition—	
H_2SO_4 61·3 per cent. ; T.N.A. 19·7 per cent. ; H_2O 19 per cent.	
H_2SO_4 consumed at retorts per ton of HNO_3 produced	1·354 tons

Efficiencies of Plants.—

Stills—(*a*) Nitric acid	96 per cent.
„ (*b*) Sulphuric acid	99 „
Retorts	95 „
Denitrators—(*a*) Nitric acid	99 „
„ (*b*) Sulphuric acid	99 „
Gaillard towers	99 „
Grillo oleum	95 „

No loss is reckoned on the mixing plant, the efficiencies of the plants being reckoned on the content of the mixed acids produced.

Recoveries of Plants.—

Stills—Average strength of nitric acid produced = 84·3 per cent. T.N.A.
„ „ sulphuric acid „ = 78·0 „ H_2SO_4.
Retorts— „ „ nitric acid „ = 86·5 „ T.N.A.
Denitrators— „ „ „ „ = 56 „ T.N.A.
„ „ sulphuric acid „ = 74 „ H_2SO_4.

Assumptions.

This balance is constructed on the assumptions that:—

1. All weak nitric acid is used for revivifying acid.
2. Consequently no stills mixed acid is prepared on the mixing plant.
3. No change is desired in the stocks of any acids.

Acids required for Nitrating Houses.

43 tons of N.G. require 114·3 tons of mixed acid,
and produce 86·2 „ spent acid.
53 „ of N.Co. require 1064·9 „ mixed acid,
and produce 1064·1 „ spent acid.

The last-named has to be divided between the mixing plant and nitric acid stills. The calculation for this division is done later. The other figures are inserted in the balance, together with the content of each mixed acid calculated from its analysis.

Acids required for N.G. Mixed Acids.

For 114·3 tons of N.G. mixed acid, we require:—

(1) 64 tons of oleum . . . . 104·5 per cent. H_2SO_4.
(2) 50·3 „ nitric acid . . . 91·8 „ T.N.A.

Normally the nitric acid for this purpose will come from the nitric acid retorts, together with the nitric acid to make up for the consumption and losses. The latter quantity is considered at a later stage. In producing 50·3 tons of strong nitric acid, the retorts will also produce weak acid.

Determination of the Amount of Weak Acid produced in preparing 50·3 tons of 91·8 per cent. T.N.A.—

Average strength of production = 86.5 per cent.
Assume a make of $100x$ tons of acid.
This represents $86.5x$ tons T.N.A.
Average strength of weak acid = 64 per cent.
Amount of weak acid produced = $100x - 50.3$ tons.
∴ T.N.A. content of weak acid produced = $(100x - 50.3) \times .64$ tons.
= $64x - 32.2$ tons.

Tabulated we get :—

	N.A.	T.N.A.	H_2O.
Strong . . .	50·3	46·2	4·1
Weak . . .	$100x - 50{\cdot}3$	$64x - 32{\cdot}2$	$36x - 18{\cdot}1$
Total . .	$100x$	$64x + 14$	$36x - 14$

$$\text{Hence } 100x \times \frac{86.5 \text{ (average strength)}}{100} = 64x + 14.$$

Whence $100x$ = 62.2 tons.

∴ Weak acid produced = 11.9 tons containing 7.6 tons T.N.A.

In this balance this is used for R.V.A., and these figures are noted for their appropriate places.

Consumption of Acids at N.G. Nitrating House.—

	Tons.	Tons H_2SO_4.	Tons T.N.A.	Tons H_2O.
Acid entering . .	114·3	66·9	46·2	1·2
Acid leaving . .	86·2	64·0	7·5	14·7
Consumption . .	...	2·9	38·7	...
Water introduced .	...	...	...	13·5

Work of Denitrators.—

The spent acid is denitrated, losing .1 ton T.N.A. (99 per cent. recovery) and .6 tons H_2SO_4 (99 per cent. recovery).

∴ Weak nitric acid produced (56 per cent.) . $= \frac{7{\cdot}4}{{\cdot}56} =$ 13·2 tons.

(This acid is used for R.V.A.)

and weak sulphuric acid produced (74 per cent.) $= \frac{63{\cdot}4}{{\cdot}74} =$ 85·7 „

(This acid goes to the concentrators.)

Water entering denitrators . . . . = 14.7 „
Water leaving denitrators (5.8 in N.A. 22.3 in S.A.) . = 28.1 „
Water introduced by denitrators . . . = 13.4 „

Water absorbed in Grillo Oleum Drying Towers.—In this balance oleum is used for drying purposes. The amount required depends upon the amount of plant working.

For the programme here considered, the requirement is 12 tons of oleum. The weak acid produced by the towers is 30 tons (66·7 per cent. H_2SO_4).

(This acid goes to the concentrators.)

12 tons of oleum contain 10.2 tons SO_3 and 1.8 tons H_2O.
30 ,, weak acid ,, 16.3 ,, SO_3 and 13.7 ,, H_2O.
∴ SO_3 absorbed = 6.1 tons.
and water ,, = 11.9 ,,

Consumption of Acids at N.Co. Nitrating House.—The consumption of acids and entry of water are calculated in the same way and inserted on the balance.

Allocation of Spent Acid to the Mixing Plant and Stills.—The figures now required are:—

(1) The amount of spent acid to be distilled.
(2) The amount of spent acid to be revivified.
(3) The amount and composition of R.V.A. to be produced.

Assume:—

(*a*) $100x$ tons of spent acid are distilled.
(*b*) $100y$,, sulphuric acid } are needed for R.V.A.
(*c*) $100z$,, oleum }

It is clear that three equations must be found connecting these three unknowns.

The stills receive $100x$ tons of spent acid containing $61.33x$ tons of H_2SO_4 and $19.73x$ tons of T.N.A.

Recovery—(1) Nitric acid (96 per cent. recovery) = $18.93x$ tons.
Average strength = 84.3 per cent.
∴ Acid produced = $22.44x$ tons.
(2) Sulphuric acid (99 per cent. recovery) = $60.72x$,,
Average strength = 78 per cent.
∴ Acid produced = $77.85x$ tons.

(The whole of the nitric acid produced is used for R.V.A.; the sulphuric acid goes to the concentrators.)

Nitric Acid Balance.

To keep the T.N.A. in the system constant, it is necessary to make a balance of the T.N.A. content of the whole of the acids to be used for mixed acids, and the content desired.

Considering the acids available for revivification, we have :—

Acid.	Tonnage.	Tons T.N.A.
Spent acid	$1064{\cdot}1 - 100x$	$210{\cdot}0 - 19{\cdot}73x$
Stills nitric acid	$22{\cdot}44x$	$18{\cdot}93x$
Retorts weak nitric acid (produced with strong for N.G. M.A.) .	11·9	7·6
Denitrators	13·2	7·4
Total T.N.A available .	...	$225{\cdot}0 - {\cdot}8x$

But the amount of T.N.A. required $= 1064.9 \times .23$

$= 244.9$ tons.

Therefore the retorts must also supply $244.9 - (225 - .8x)$ tons to keep the T.N.A. in the system constant, *i.e.*, $19.9 + .8x$ „

Since the average strength of the acid produced $= 86.5$ per cent.

∴ The amount of acid required from the retorts is $\frac{19.9 + .8x}{.865}$ tons.

$= 23 + .92x$ tons.

Three Equations.

In practice the whole of the acids used for producing nitro-cotton mixed acid are tabulated and equated to the mixed acid produced. The above step is inserted to show how the additional amount of nitric acid from the retorts is found.

The complete tabulation thus becomes :—

Kind.	Tons.	Tons H_2SO_4.	Tons T.N.A.	Tons H_2O.
Spent	$1064{\cdot}1 - 100x$	$652{\cdot}6 - 61{\cdot}33x$	$210 - 19{\cdot}73x$	$201{\cdot}5 - 18{\cdot}94x$
Stills, nitric acid . .	$22{\cdot}44x$	...	$18{\cdot}93x$	$3{\cdot}51x$
Retorts, weak nitric acid (produced with strong for N.G. M.A.) .	11·9	...	7·6	4·3
Additional retorts, nitric acid (average strength)	$23{\cdot}0 + {\cdot}92x$	...	$19{\cdot}9 + {\cdot}8x$	$3{\cdot}1 + {\cdot}12x$
Denitrators, weak nitric acid	13·2	...	7·4	5·8
Sulphuric acid . .	$100y$	$93y$	...	$7y$
Oleum	$100z$	$104{\cdot}5z$	...	$-4{\cdot}5z$
Total . . .	$1112{\cdot}2 - 76{\cdot}64x$ $+ 100y + 100z$	$652{\cdot}6 - 61{\cdot}33x$ $+ 93y + 104{\cdot}5z$	244·9 ...	$214{\cdot}7 - 15{\cdot}31$ $+ 7y - 4{\cdot}5z$
N.Co., mixed acid required . . .	1064·9	661·8	244·9	158·2

The T.N.A. column has been made to balance as indicated in the previous paragraph.

The water column is merely a difference column, hence only two equations have been determined. Using the first two columns we get:—

$$\begin{aligned} 1112.2 - 76.64x + 100y + 100z &= 1064.9 \\ \text{I. } \textit{i.e.},\ 76.64x - 100y - 100z &= 47.3 \\ 652.6 - 61.33x + 93y + 104.5z &= 661.8 \\ \text{II. } \textit{i.e.},\ 61.33x - 93y - 104.5z &= -9.2 \end{aligned}$$

Sulphuric Acid Balance.

The third equation is obtained by balancing the H_2SO_4 over the whole system. The total H_2SO_4 required is:—

(1) That consumed at the Retorts.
(2) That required as feed acid for the Grillo Oleum Plant.
(3) That required for mixing.

This acid has to be delivered from the Concentrators, their receipts being:—

(*a*) Weak acid from the Denitrators.
(*b*) ,, ,, Grillo drying towers.
(*c*) ,, ,, Stills.

H_2SO_4 Consumption at Retorts.—

H_2SO_4 consumed per ton of T.N.A. produced = 1.354 tons.
T.N.A. produced by Retorts = $(46.2 + 7.6 + 19.9 + .8x)$.
H_2SO_4 required = $(73.7 + .8x)\ 1.354$.
= $99.8 + 1.08x$ . . . . (1)

H_2SO_4 required as Feed Acid at Grillo.—Particulars of oleum requirements are:—

Required for	Tons Oleum.	Tons H_2SO_4	Tons H_2O.
N.G. mixed acid . . .	64·0	66·9	$-2·9$
N.Co. mixed acid . . .	100z	104·5z	$-4·5z$
Grillo drying towers . .	12·0	12·5	$-0·5$
Total . . .	76 + 100z	79·4 + 104·5z	$-3·4 - 4·5z$

The object of the Grillo plant is to add SO_3 to feed acid to form oleum. In doing this it also produces SO_3 which is absorbed in the drying towers; this is allowed for in paragraph 3, and it produces SO_3 (and SO_2 which remains unconverted) which are lost. This loss must be allowed for in calculating the sulphur required, but as it does not enter the system, no provision is made for it actually in this calculation. Consideration of SO_3 absorbed by feed acid to form oleum,

Assume $100a$ tons of feed acid are required—

This contains $93a$ tons of H_2SO_4, and has to produce $76 + 100z$ tons of oleum (as in above table).

$\therefore$ SO_3 absorbed $= 76 + 100z - 100a.$

This expressed as $H_2SO_4 = (76 + 100z - 100a)\frac{98}{80}\left(\text{since } \frac{H_2SO_4}{SO_3} = \frac{98}{80}\right)$

$= 93.1 + 122.5z - 122.5a$ tons.

Also H_2SO_4 content of oleum produced $= 79.4 + 104.5z$ tons.

But H_2SO_4 content of feed acid $= 93a$ tons.

$\therefore$ Gain in H_2SO_4 content $= 79.4 + 104.5z - 93a$ tons.

This gain in H_2SO_4 is due to SO_3 absorbed and therefore must equal this amount expressed as H_2SO_4.

Thus $93.1 + 122.5z - 122.5a = 79.4 + 104.5z - 93a$

Whence $93a = 56.74z + 43.2$ . . . . . (2)

This is expressed in this form as the equations are to be based on H_2SO_4 content, and $93a$ is the H_2SO_4 content of the feed acid required.

H_2SO_4 required for Mixing.—The sulphuric acid required for mixing $= 93y$ tons H_2SO_4 . . . . (3)

H_2SO_4 Usage at Concentrators.—The Concentrators receive :—

	Tons	H_2SO_4.	H_2O.	
Ex-Denitrators .	85·7	63·4	22·3	p. 432
Ex-Grillo . .	30	20	10	p. 433
Ex-Stills . .	77·85x	60·72x	17·13x	p. 433
Total. .	115·7+77·85x	83·4+60·72x	32·3+17·13x	

Recovery $=$ 99 per cent. H_2SO_4.

H_2SO_4 produced $= 82.6 + 60.11x$.

Total H_2SO_4.—Summing the requirements of H_2SO_4 over the whole system :—

(1) For Retorts .	$99.8 + 1.08x$
(2) For Grillo . .	$43.2 + 56.74z$
(3) For R.V.A. .	$93y$
Total . .	$143.0 + 1.08x + 56.74z + 93y$

Thus :—

$$82.6 + 60.11x = 143.0 + 1.08x + 56.74z + 93y$$

$$\text{III.} \quad \therefore \quad \underline{59.03x - 93y - 56.74z = 60.4}$$

and this is the third equation.

Solution of Three Equations.

We now have to solve :—

$$\begin{aligned} \text{I.}\ & 76.64x - 100y - 100z = 47.3 \\ \text{II.}\ & 61.33x - 93y - 104.5z = -9.2 \\ \text{III.}\ & 59.03x - 93y - 56.74z = 60.4. \end{aligned}$$

Ordinary algebraic methods give the following solutions :—

$$100x = 347.0$$
$$100y = 56.2$$
$$100z = 162.4$$

Completion of Acid and Water Balance.

Having obtained these figures the acid and water balance may be completed :—

Spent acid to stills = 347.0 tons.
∴ Spent acid for revivification = 717.1 tons.

Their respective contents are worked out and inserted.

The loss at the stills is (*a*) 2.8 tons T.N.A.

∴ T.N.A. produced = 65.7 tons contained in 77.9 tons of average strength acid.

(*b*) 2.1 tons H_2SO_4

∴ H_2SO_4 produced = 210.7 tons contained in 270.1 tons of 78 per cent. acid.

The extra nitric acid produced at the retorts is 22.7 tons T.N.A.

This is produced as 21.6 tons of strong acid
4.6 tons of weak acid.

The 4.6 tons (containing 2.8 tons T.N.A.) is accordingly added to the 11.9 tons already noted (p. 432).

Oleum required for R.V.A. = 162.4 tons.
Sulphuric acid required for R.V.A. = 56.2 tons.

This is split up as follows:—

(*a*) 36.2 tons are used in the manufacture of R.V.A.

(*b*) 20 tons (approximately 2 per cent. of the nitro-cotton mixed acid produced) are used direct for the revivification process.

The R.V.A. accordingly consists of:—

Acid.	Tons.	H_2SO_4.	T.N.A.	H_2O.
Oleum	162·4	169·7	...	- 7·3
Sulphuric acid	36·2	33·7	...	2·5
Retorts, strong nitric acid . . .	21·6	...	19·9	1·7
Retorts, weak nitric acid . . .	16·5	...	10·4	6·1
Stills, average strength nitric acid .	77·9	...	65·7	12·2
Denitrators, weak nitric acid . .	13·2	...	7·4	5·8
R.V.A.	327·8	203·4	103·4	21·0
Percentage composition . . .	...	62·1	31·5	6·4

This gives the amounts of acids (and their origin) to which the Mixing Plant will work.

It is necessary at this stage to check the working to ascertain that:—R.V.A. plus Spent Acid plus Sulphuric Acid = the required Mixed Acid. This may be done by the following tabulation:—

Acid.	Tons.	H_2SO_4.	T.N.A.	H_2O.
Desired mixed acid	1064·9	661·8	244·9	158·2
Spent acid	717·1	439·8	141·5	135·8
R.V.A.	327·8	203·4	103·4	21·0
Sulphuric acid	20·0	18·6	...	1·4
Mixed acid produced	1064·9	661·8	244·9	158·2

Sulphuric Acid Balance.—

Acid entering Concentrators.	Tons.	H_2SO_4.	H_2O.
From stills	270·1	210·7	59·4
From denitrators	85·7	63·4	22·3
From Grillo.	30·0	20·0	10·0
	385·8	294·1	91·7
Loss H_2SO_4.		2·9	
Acid produced 93 per cent. . .	313·1	291·2	21·9
∴ Water expelled. . . .			69·8

The distribution of acid is calculated from the equations dealing with sulphuric acid.

The Grillo Plant requires	135·3 tons H_2SO_4
The Mixing Plant requires	103·6 ,, ,,
The Nitric Acid Retorts require	52·3 ,, ,,
Total requirements	291·2 tons H_2SO_4

This is the production of the Concentrators.

SO_3 Production for the System by the Grillo Plant.

Oleum produced	238·4 tons
Feed acid entering	145·5 ,,
∴ SO_3 added	92·9 ,,
SO_3 absorbed in system	6·1 ,,
∴ Production	99·0 tons

This requires 22·3 tons of water to be absorbed from the system to become 121·3 tons of H_2SO_4 (100 per cent.).

The H_2SO_4 shown on the balance as lost and consumed is:—

Nitro-cotton Nitration	9·2 tons
Stills	2·1 ,,
Nitro-glycerine Nitration	2·9 ,,
Denitrators	·6 ,,
Concentrators	2·9 ,,
Retorts	103·6 ,,
	121·3 tons

Thus no additional H_2SO_4 is added to the system.

Water Balance.—

Water entering at:—

Nitro-cotton Nitration House	43·3 tons
Stills	5·9 ,,
Nitro-glycerine Nitration House	13·5 ,,
Denitrators	13·4 ,,
Retorts	4·1 ,,
Grillo	11·9 ,,
	92·1 tons

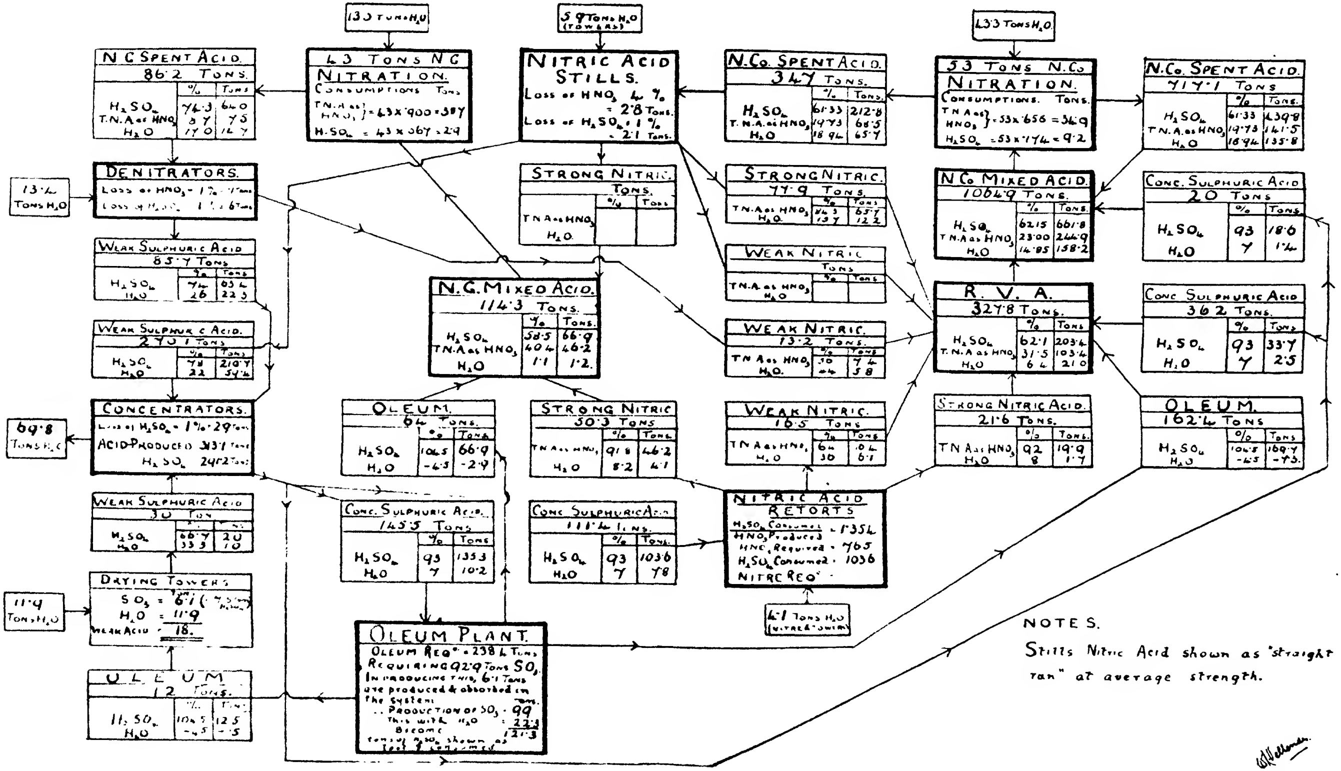
Water leaving system at Concentrators	69·8 tons
Negative water content produced at Grillo	22·3 ,,
	92·1 tons

Thus the statement produced is an acid and water balance, the acid being kept of constant amount and dilution.

Alternative balances may be prepared in a similar manner—

(*a*) Showing different methods of treatment of acids.
(*b*) Altering stocks of acids.
(In practice it is often found that the stock of one kind of acid may become too large or too small.)
(*c*) Showing the effect of varying the degree of sulphuric acid concentration.

By a comparison of the balances produced the costs of each system of working may be compared.



NOTES.

Stills Nitric Acid shown as "straight tan" at average strength.

FIG. 132.—An Acid and Water Balance.

N. A. & N.

(Face page 440.

INDEX OF NAMES

INDEX OF SUBJECTS

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