Birla Central Library
PILANI (Rajasthan)

Class No :- 546.78
Book No :- L578T
Accession No :- 37170

TUNGSTEN

Its History, Geology, Ore-Dressing, Metallurgy, emistry, Analysis, Applications, and Economics

by

K. C. LI, M.E., A.R.S.M.

Governor, Commodity Exchange, New York
Chief Engineer, Tungsteno Mexicano, S.A., Mexico.
Chief Engineer, National Reconditioning Company, Inc., New York
Chairman of the Board, Wah Chang Trading Corporation, New York

and

CHUNG YU WANG, M. INST. M.M.

University Medalist, Columbia University
Technical Expert, Ministry of Economic Affairs, China
Director of Research, National Reconditioning Company, Inc., New York

A. C. S. Monograph No. 94

Second Edition, Revised and Enlarged

REINHOLD PUBLISHING CORPORATION
330 West Forty-second St., New York 18, U. S. A.
1947

First Edition
Copyright 1943 by
REINHOLD PUBLISHING CORPORATION

Second Edition
Copyright 1947 by
REINHOLD PUBLISHING CORPORATION

All rights reserved

Printed in U. S. A. by
WAVERLY PRESS, BALTIMORE, MD.

GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abbegg's and Gmelin-Kraut's Handbuch der, Anorganischen Chemie, Moissan's Traité de Chimie Minérale Générale, Friend's and Mellor's Textbooks of Inorganic Chemistry and Heilbron's Dictionary of Organic Compounds, it often takes a great deal of time to coordinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monographs, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

AMERICAN CHEMICAL SOCIETY

BOARD OF EDITORS

F. W. WILLARD, *Editor of Monographs*

Scientific Series:—
S. C. LIND,
W. MANSFIELD CLARK,
LINUS C. PAULING,
L. F. FIESER.

Technologic Series:—
WALTER A. SCHMIDT,
E. R. WEIDLEIN,
W. G. WHITMAN,
THOMAS H. CHILTON,
BRUCE K. BROWN,
W. T. READ,
CHARLES ALLEN THOMAS.

Preface to Second Edition

The present edition has been revised by the addition of more recent material to all the chapters, particularly to those on "The Geology of Tungsten" and "The Industrial Application of Tungsten."

In the treatment of Ferrous Alloys of Tungsten the authors have freely made use of the book, *Tool Steels* by J. P. Gill, as well as of his recent article in "German Tungsten Tool Steels." In the preparation of the list of some of the commercial ferrous and non-ferrous tungsten alloys, Woldman and Metzler's *Engineering Alloys* has been largely drawn upon. With regard to other new material used in the revision, due acknowledgments have been made in the appropriate places.

The authors wish to express their appreciation to Miss Jill M. Sternberg of the Editorial Department of the Reinhold Publishing Corporation, for her cooperation in the preparation of this edition.

K. C. Li
C. Y. Wang

New York, N. Y.
October 31, 1946

Acknowledgements

The authors gratefully acknowledge their indebtedness to those who have made valuable suggestions and comments on the manuscript and to those who have helped in its preparation. Dr. Zay Jeffries has read through the chapter on Chemistry; Mr. E. A. Lucas and Mr. G. C. Wheeler have made comments on the chapter on Metallurgy; Dr. Frank L. Hess has permitted use of his notes on the occurrences of tungsten deposits and the maps illustrating them; Mr. Carl M. Dice has read through the chapter on Ore-Dressing; both Mr. H. K. Masters and Mr. G. G. Hawley have read the proofs; both Mr. Jack Van Fleet and Dr. H. B. North have drawn the authors' attention to some new uses of tungsten; Mr. Kechin Hsu has consented to the use of his thesis on the tungsten deposits of Kiangsi.

Thanks are due to Messrs. Chapman and Hall, Ltd., for permission to quote and to make use of the drawings from "Tungsten" by Colin J. Smithells, to the McGraw Hill Book Publishing Company, Inc., for permission to quote from "Strategic Mineral Supplies" by G. A. Roush, to John Wiley & Sons for permission to quote from "Steel and Its Heat Treatment" (1935 Edition) by D. K. Bullens, and to Dr. Walter C. Mendenhall for use of the illustrations of the tungsten minerals, as described by Dr. Frank L. Hess in U. S. G. S. Bulletin 652.

K. C. Li
C. Y. Wang

New York, N. Y.

Foreword

Tungsten is a rare and comparatively new metal. It is one of the most important, if not the most strategic, of war metals. Its use in the manufacture of high-speed steel was not perfected until 1914 when the World War I began.

Before 1914 it was the belief of some Allied military experts that in six months Germany would be exhausted of ammunition. The allies soon discovered that Germany was increasing her manufacture of munitions and for a time had exceeded the output of the Allies. The change was in part due to her use of tungsten high-speed steel and tungsten cutting tools. To the bitter amazement of the British, the tungsten so used, it was later discovered, came largely from their Cornish Mines in Cornwall.

In the summer of 1913 when I was a student under Professor S. J. Truscott, famous author of "Text Book of Ore Dressing," at the Royal School of Mines, Imperial College, London, I was assigned work on magnetic separation, at Redruth, Cornwall, where the tin concentrates generally contain 2 to 3 per cent wolframite, the most important tungsten bearing mineral.

One day Professor Truscott inspected the Separation Room. He asked how I was progressing. I told him I had gotten quite a bit of the wolframite out. As I presented my "production" to him I queried, "What will be done with the wolframite after it is recovered?"

"Oh," Professor Truscott quickly replied, "We send this to the Germans who somehow or other know how to make use of this blooming stuff."

"At what prices?" I asked.

"We are getting 8 to 10 shillings per unit," the Professor answered.

This was about one year before World War I broke out.

On my return to London from the Cornish mines, I showed Professor Truscott a mineral crystal which I had brought with me from China. I informed him that it was wolframite, and that the Cornish mines had no such large crystals. Professor Truscott commented, "It is rather a nice specimen, is it not?" and showed no further interest.

With the discovery that the Germans were effectively using tungsten in the manufacture of ammunitions, there started the scramble for tungsten. An immediate effect was the rise in the price of tungsten to almost one hundred dollars a unit in the United States. I lost no time in hurrying back to China.

It is perhaps appropriate to relate here how the world's greatest source of tungsten was discovered thirty-two years ago. Like so many other discoveries, the discovery of tungsten in China was also an accident.

In 1911 I was commissioned to explore for tin in the Southwestern part of China. Among the many places I explored and surveyed was Yao Kang Sein in the lofty mountain range of Wuling, located at the intersection boundary point of the Chi-Chang, Yu-Chen and Tze-Hsing districts of Hunan.

One cold evening in the month of May, after a day's hard prospecting, I stopped over at the Wayside Inn in Ta-Ling, which was located at an elevation of about six thousand feet. While the Innkeeper's wife and daughter were cooking supper, I made myself useful in the kitchen, which also served as my bedroom, where my canvas cot was spread. I was asked by the Innkeeper's daughter to watch the stove which stood prominently at a corner of the room. The stove burned fresh wood —the only fuel available and it was my duty not only to fire the stove but to keep it burning. The ventilation being poor, I had to blow by the mouth in order to keep the fire in steady flame. When I became exhausted, I was relieved by the Innkeeper's daughter, Hsiao-mei.

In the course of my "windy" efforts, I was intrigued by the characteristics of the stove. I asked Hsiao-mei who was just in her teens how long the stove had been in use, and when and how it was built. Hsiao-mei, thinking I was trying to take an interest in her, blushed and stammered that she did not know. From her mother I learned that the stove was built the year she was married and that for the past twenty-five years it required no repairs.

The next morning I asked the husband about the origin of the material which he used to construct his twenty-five year old stove. Leading me to his back garden situated on the slope of the hill, he pointed to a huge outcrop formation and complained that ever so often huge chunks would unloosen themselves, roll down the hill, and ruin his crop. His remedy, he said, was to convert the offending stones into some practical utensil. He converted them into foundations for his cesspool, into tools for his garden, into slabs for his sidewalk, and into many other useful articles that required the use of stone. The Innkeeper was obviously proud of his accomplishments.

I could not see the outcrop clearly because of fog and the mist which covered the mountain range. I climbed to the outcrop, and after a cursory examination I concluded that it was well mineralized though not with the tin-bearing mineral, cassiterite, for which I was commissioned to prospect. I was impressed by the size of the outcrop and especially by the weight of the mineral. Among the specimens I gathered was a lovely egg-shaped specimen, especially treasured by me, because it was handed to me by Hsiao-mei. For years I used and still use it as a paper weight.

On my return to China in 1915, I hastened to Ta-Ling, sought out the Innkeeper of the Wayside Inn, and informed him of the value of his property. He would not believe me. I inquired about Hsiao-mei. I was told she had married but on learning that I was arriving, she hurried home to see the "returned student" from England.

A mining company, the Yu Hou Tungsten Mining Company, was immediately organized to acquire the adjoining property. In December, 1915, the Yu Hou Tungsten Mining Company made the first shipment of tungsten ore from China. This shipment was consigned to the United States.

Export duty on all shipments from China was then 5 per cent ad valorem. As there was no wolframite market in China there was no market value attached to wolframite. The superintendent of the Chinese Maritime Customs at Changsha was asked to put an arbitrary value. To meet the requirements of customs declaration, I decided to apply the Chinese word "Wu" to designate the name of the mineral I was shipping.

Despite my arguments, the superintendent, Oxford-trained and rather bureaucratic, refused to pass the material as "Wu." He decided on the word "Huk Sha," which means "black sand." An "arbitrary" value of 100 Chinese dollars per ton, then equivalent to 75 American dollars, was placed on this "black sand," thus making the export duty 5 Chinese dollars or U. S. $3.75 per ton.

As a mining engineer I protested the classification of the product as "black sand" and insisted that it be classified as a tungsten-containing mineral. I filed my protest with the Inspectorate General of Customs in Peking, and petitioned him that my coined word "Wu" be used in future in the Customs declaration as the official designation. Several shipments of tungsten concentrates were shipped from China as "black sand" before my recommendation was accepted by the Inspectorate General of Customs and the word "Wu" has since become the official Customs designation for wolframite.

The first shipment of Chinese tungsten ore, which came from the eluvial deposits, was assayed by Ledoux & Company to contain the purest wolframite ever mined in any part of the world. It contained WO_3 as high as 78.80 per cent, with practically no impurities of any kind. The first shipment was delivered to the Bethelehem Steel Company. The second shipment was delivered to the United States Steel Company.

Following these two shipments, made by the Yu Hou Tungsten Mining Company, China became reputed as a country with large deposits of almost pure tungsten ore. Steel companies in England and in the United States demanded more and larger shipments from China, with the result that a host of American engineers departed for China in search of tungsten. All American firms with business connections in China directed their representatives to ship tungsten ore from China. The American Express Company, C. E. Richardson & Co. of Hong Kong, Mr. Ralph Weymouth, and others followed the example of Yu Hou Tungsten Mining Company, and became miners and exporters of tungsten ore.

News of my discovery of tungsten ore in Yao Kang Sein, with the help of an Innkeeper's daughter, spread rapidly from Hunan province to other provinces in China: Kiangsi, Kwangtung, Kwangsi, Yunnan, and finally to other countries: French Indo-China, and Siam.

Since 1915 China has become recognized as the world's largest producer of tungsten which position she will undoubtedly hold for many years to come since her reserves have been estimated to amount to approximately ten billion pounds of WO_3.

Tungsten, like antimony, in making China known as a rare metal producing country, has meant millions of dollars to the National Treasury of the young Chinese Republic. Tungsten was used as security for the several large China loans arranged by the United States before the Pearl Harbor incident and before the Lend-Lease Act.

It was because of tungsten that Japan had her Axis partner, Germany, dictate to Vichy the removal of the French Governor General of Indo-China, General Georges Catroux, and the appointment as Governor, of Admiral Jean Decoux, who would "cooperate" with Japan in the matter of the very large tonnage of tungsten ore stored and owned by the Chinese Government in French Indo-China ready for export. In June, 1940, I urged the American Government to acquire this Chinese owned tonnage in French Indo-China through the then Federal Loan Agency Administrator, Jesse H. Jones. Mr. Jones, sensing the crisis in French Indo-China, was quick to act on my suggestion. The transaction was completed in twenty-four hours, no doubt one of the quickest transactions of such magnitude ever consummated between two nations.

The American Consul-General Reed at Hanoi, acting on the explicit and urgent instructions of Secretary of State, Cordell Hull, secured from Governor-General Georges Catroux the immediate written release for export to America of the tungsten cargo as American-owned property. Consul-General Reed cabled the State Department within twelve hours that the release was secured from Governor-General Georges Catroux and the Chairman of the United States Maritime Commission in Washington, Rear Admiral Emory S. Land, ordered the immediate dispatch of four "special vessels," SS Birmingham City, SS Puerto Rican, SS Oregonian and SS Chickasaw City, to load the tungsten from French Indo-China for America. The captains of these four vessels on arrival at Staten Island, New York, reported that the Japanese were so furious that their cruisers followed them for three days after they left the French Indo-China waters.

In the 100 million marks revolving barter agreement of July 25, 1936, between China and Germany, tungsten headed the list of Chinese raw materials to be bartered. Hitler's Defense Minister, Colonel General Werner Fritz Von Blomberg, conducted the negotiations, and General Von Reichnau, Herr Oberst Thomas, and General Von Seeckt, then chief German advisor of Generalissimo Chiang Kai-shek, also participated. General Von Reichnau made a special trip to China as Hitler's representative.

In 1936, the Chinese, like the English and American economists, did not believe that Germany was stockpiling tungsten for the present war. Rather, like the English and Americans, they feared that the Germans would dump the Chinese tungsten ore so bartered on the open market in order to get foreign exchange, and in this way ruin the tungsten market. Von Blomberg was approached on agreeing not to dispose of any Chinese tungsten ore so bartered in the open market. Von Blomberg chuckled with satisfaction and said, "Well, sir, you need not worry about that. You write a letter to that effect and I will sign it."

From 1936 to 1940 "Germany kept her word." Not a pound of bartered Chinese tungsten ore reached the German or the world market as had other raw products bartered through China and other countries.

In addition to the stockpile of bartered tungsten ore, Germany brought, cleverly and quietly, huge tonnages of Chinese tungsten ore from elsewhere during the years 1936, 1937, 1938, 1939, and up to the very moment of the outbreak of war in Europe when shipment from some areas was impossible. In 1940 and 1941 Germany was purshasing tungsten from Bolivia, Argentina, Peru, Mexico, and the United States through her Axis partner, Japan, then regarded as "neutral" by North and South American countries. Even after Pearl Harbor, a Japanese steamer from South America was captured by the United States with a shipment of tungsten ore from one of the South American countries destined for Germany. The Japanese steamer "Wilimoto" was renamed "Oldenwald" in mid-ocean for this purpose.

Quite recently Germany has been purchasing tungsten ore in Portugal and Spain at prices as high as $50,000 per ton of ore. The Americans and British countered with preclusive purchasing on the theory that one pound of tungsten in the hands of the Allies in Portugal and Spain means one pound of tungsten less in the hands of Germany.

Prior to World War II, off-grade tungsten ore, particularly that from South America and Mexico, seldom found a market elsewhere except in Germany. A purchasing pool in Berlin headed by the able tungsten expert, Herr Hermann C. Starck, stockpiled at considerable discount practically the entire world output of the offgrade ore. Virtually none of this off-grade ore from South American countries has been shipped to the United States in the years prior to World War II.

Realizing that the China supply of tungsten would be interrupted in the event of war in the Pacific, I urged the American Government, as early as August 1940, to buy up the entire South American production of tungsten ore regardless of quality. To implement my recommendation an ore concentration plant was erected in the Foreign Trade Zone, Staten Island, New York, known as the National Reconditioning Company, capable of purifying all kinds of off-grade tungsten ores from any part of the world.

By providing an outlet for off-grade South American tungsten ores in the United States it was felt that the incentive of Latin America to sell to Germany direct or through Japan would be removed. The United States Treasury, acting on the advice of the Advisory Council of National Defense, endorsed the recommendation to purchase off-grade South American tungsten ores, and a purchase contract for a large tonnage was granted.

One month later I sailed for South America and I visited the mining centers of Bolivia, Peru, Argentina and Brazil. I acquired for the United States Government all available production of off-grade South American tungsten ores. This acquisition marked the beginning of all subsequent tungsten contracts between the United States Government and the South American countries.

Though the Mexican production of tungsten has not been large, a buying and concentration station has been established in Nogales, Sonora, under the name of Tungsteno Mexicano, S.A., whose purpose is to stimulate the production in Mexico and so help the war effort. In this way the prospect of increased shipments from good neighbors in Latin America has been advanced.

The large shipment from China together with the concentrates from South America that had been purified in 1940 constituted such a pre-Pearl Harbor stockpile that the possibility of shortage of this strategic material for the duration has been eliminated. Even at the height of American consumption for the war effort, it has been unnecessary to disturb the pre-Pearl Harbor stockpile. This factor has enabled both producers and consumers to plan their production and consumption with confidence.

The tungsten industry is still in its infancy. Despite developments made during two World Wars, it is a mistake, I think, to assume that tungsten is only a strategic material. Besides its use in high speed steel, cutting tools, colors, lamp filaments, radio tubes, x-rays, catalysts, camera lens, I am of the opinion that there are many other fields in which tungsten can well be used. It is for this reason I have invited my former professor Dr. C. Y. Wang, author of the only treatise in English on Antimony, to collaborate with me in the preparation of this book which, I hope, will stimulate the interest of those who share my own optimistic feeling toward the future of tungsten.

K. C. Li

New York, N. Y.
July 7, 1943

Contents

Chapter I

The History of Tungsten

The word *tungsten* is derived from the Swedish words *tung*, meaning heavy or ponderous, and *sten*, meaning stone; it was first used by A. F. Cronstedt in 1755. As to the origin of the word *wolfram*, it has been variously explained. The earliest mention of *wolferam* in literature was made by Lazarus Ercker in 1574. Its spelling has gone through many modifications: *wolfert, wolfort, wolfart, wolffert, wolfrig, wolffram, wolferan, wolferam, wolfish, woolfram, wolframit,* and *wolframicum.* It was suggested that the word originates from the German words *wolf*, meaning a beast of prey, and *ram*, froth. Later, in 1820, A. Breithaupt in his book "Kurze Charakteristik des Mineralsystems" finally adopted the word *wolframite* for the mineral containing the tungstate of iron and manganese.

The writers of the period before 1781 had very vague ideas as to the composition of the mineral they so named. Both scheelite and wolframite were at one time considered to be ores of tin. The tin miners of Cornwall named the mineral *cal* or *call*, or mock-lead, and regarded it as a harmful ore because "it eats up tin as a wolf eats up sheep." J. F. Henckel regarded wolfram as an arsenical and ferruginous ore of tin; J. G. Wallerius and A. Cronstedt, as a manganese ore containing tin and iron; J. H. G. von Justi, as an ore containing iron, arsenic, tin and non-metallic earth; and J. G. Lehmann, as a glassy earth containing iron and tin.

It was not until 1781, when C. W. Scheele, in his memoir, "Tungsten beständs-delar", made clear the nature of the composition of tungsten ore (scheelite) which he showed to be a compound of lime with a peculiar acid, that the discovery of a new element was in the offing. Later, in 1821, C. C. Leonhard, in his "Handbuch der Oryktognosie", honored C. W. Scheele by naming the mineral (a calcium tungstate) with which he experimented *scheelite.*

In 1783 the two brothers, J. J. and F. de Elhuyar, one of whom at least had worked under C. W. Scheele, published their memorable work, *Analisis quimico del volfram y exámen de un nuovo metal que entra en su composicion,* in which they showed that they had isolated the element, and that in wolfram that element is associated with manganese and iron instead of calcium. Perhaps C. W. Scheele might have already prepared the metal; but the fact remains that "the first published account of the isolation of the element is that of the Spaniards, J. J. and F. de Elhuyar". Thereafter, workers in increasing number investigated the properties and applications of this new element. As early as 1786 H. I. Duhamel du Monceau ("Encyclopedie méthodique", Paris, Vol. 1) emphasized the possibility of the use of tungsten to harden steel, and also in the same year the brothers de Elhuyar demonstrated that "it formed with pig iron a dense, greyish-white, hard and brittle combination". F. Wöhler produced the so-called tungsten bronze and recognized its application.

The year 1847 is significant in that it marks the date when the industrialization of tungsten may be said to have begun. In that year R. Oxland took out British Patent No. 11848 for the manufacture of sodium tungstate and tungstic acid, which forms the starting point of the metallurgy of tungsten.

According to Gruner, the first attempts to produce tungsten steel were made in 1855 by J. Jacob and Koeller, who obtained patents in France. Subsequently, various investigators took an interest in the problem. Oxland in 1857 took out a patent (No. 2114) for the production of tungsten steel. In 1857 Mushet patented a number of methods of producing tungsten steel, and in 1868 put out an air-hardening or self-hardening steel, containing about 5 to 8 per cent of tungsten. Prof. A. Delvaux de Feneffe of Liège University in 1860 described a process on "Purification de l'etain et emploi du tungstène par l'amélioration de l'acier et de la fonte de fer". The first practical application of tungsten steel was in the form of rails made at Terre Noire in 1868. In 1886 Dr. G. Heppe wrote an article in *Stahl und Eisen* on "The Industrial Application of Tungsten and its Connections", and in 1897 Prof. V. Leepin of St. Petersburg carried out a number of tests on the mechanical properties of tungsten and molybdenum steel. Tungsten high-speed tool steel first came to the attention of the general public when, at the Paris Exposition of 1900, Bethelehem Steel Company exhibited the use of tungsten-steel alloy as tool steel. Although it may be disputed that Taylor and White invented the high-speed tool, yet they may be credited with its development. It was between 1904 and 1906 that vanadium was first incorporated into the composition of modern high speed steels.

In 1904 Just and Hannaman patented a process for drawing tungsten filaments by mixing the finely divided metal powder with an organic binder. But it was not until 1909, when Coolidge took out his first patent, that the development of tungsten filament began.

The extreme hardness of tungsten carbide, WC, has been known for a long time, but its brittleness delayed its introduction into practical service. The problem could not be considered technically solved until 1927, when the Krupp Laboratory at Essen discovered that, if tungsten carbide is mixed with a bonding or cementing material, a very serviceable product is obtained.

References

Gill, J. P., "Tool Steels", p. 5-10, American Society for Metals, Cleveland, 1944.

Gmelin's, "Handbuch der anorganischen Chemie", System Number 54, p. 1-3 (Wolfram), Verlag Chemie, Berlin, 1933.

Hadfield, R. A., "Alloys of Iron and Tungsten", Part I: Origin of the Name and Discovery of the Metal, *Journal Iron & Steel Inst.*, LXIV, 14-44, 1903.

Koppel, I., "Beitrage zur Entdeckungsgeschichte des Wolframs", *Chem. Ztg.*, **50**, 117 (1926).

Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. **XI**, p. 673-675, Longmans, Green & Co., New York, 1931.

Chapter II

The Geology of Tungsten

I. GENERAL DESCRIPTION OF THE DEPOSITS

It has not been found that tungsten exists in its elemental form in nature. Compared with other useful elements, it is a rare element. It has been calculated by F. W. Clarke and H. S. Washington that the average proportion of tungsten in the igneous rocks of the earth's crust is 5×10^{-5} per cent, and according to W. Vernadsky it is 0.000048 per cent. In the order of abundance in the earth's crust, tungsten is rated, in the Clarke and Washington table, as the twenty-sixth element. Taking aluminum, the most abundant metal, as 100, C. H. Mathewson gives 0.06 for tungsten. Its production, relative to that of the other metals, can be gleaned from the following table, taking for comparison the 1938 production and the tungsten tonnage as a unit:

Steel (Ingots, Castings)	1/6000	Antimony	1/2
Pig Iron (including Ferro-alloys)	1/5400	Magnesium	1/1.5
Manganese	1/150	*Tungsten*	*1*
Copper	1/117	Molybdenum	1
Lead	1/100	Silver	2
Zinc	1/90	Quicksilver	3
Aluminum	1/34	Zirconium	3
Chromium	1/20	Cadmium	4
Tin	1/8	Vanadium	5
Nickel	1/7	Gold	17
Titanium	1/6	Bismuth	17

Explanation: For instance, the yearly production of tungsten is 1/100 that of lead and 17 times that of gold.

It will then be seen that, although tungsten is an important strategic metal, it ranks fourteenth in the order of production of the most essential metals used in the industries today.

Tungsten Minerals

Tungsten minerals can be conveniently divided into two groups: the wolframite group, and the scheelite group:

(1) The wolframite group contains three minerals: ferberite, wolframite, and hübnerite. Quoting Hess and Schaller[1]:

"**Ferberite:** A monoclinic iron tungstate having the composition $FeWO_4$ when pure. It may contain not more than 20 per cent of the hübnerite molecule, $MnWO_4$.

"**Hübnerite:** A monoclinic manganese tungstate having the composition $MnWO_4$ when pure. It may contain not more than 20 per cent of the ferberite molecule, $FeWO_4$.

"**Wolframite:** A monoclinic mineral containing the ferberite molecule

($FeWO_4$) and the hübnerite molecule ($MnWO_4$) in all proportions between 20 per cent $FeWO_4$ and 80 per cent $MnWO_4$ and 80 per cent $FeWO_4$ and 20 per cent $MnWO_4$".

First wolfram specimen discovered in China. Exact size. (See Foreword.)

These three minerals form a continuous series of iron-manganese tungstates, of which the iron end is ferberite, and the manganese end is hübnerite. In fact, pure ferberite and pure hübnerite are not found as such in nature.

The physical and chemical properties of these three minerals are[2]:

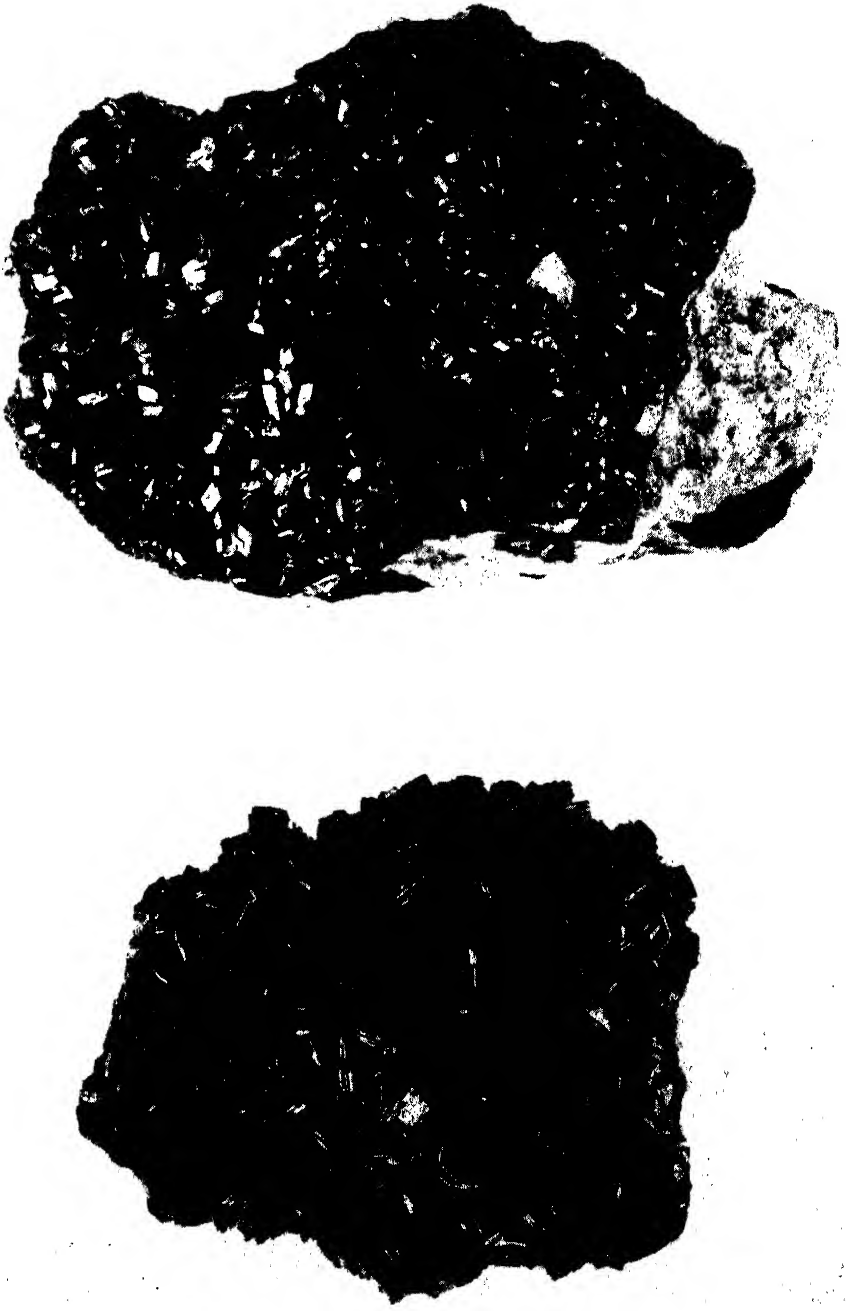
	Ferberite	Wolframite	Hubnerite
Composition (pure)	$FeWO_4$	(Fe, Mn) WO_4	$MnWO_4$
WO_3 and W (%)	76.3; 60.5	76.5; 60.6	76.6; 80.7
Mn (%)	0+	3.6–14.5	18.1-
Fe (%)	18.4-	3.7–14.7	0+
Crystallization	Monoclinic	Monoclinic	Monoclinic
Cleavage	Perfect in 1 direction	Perfect in 1 direction	Perfect in 1 direction
Specific gravity	7.5	7.1–7.5	7.2–7.3
Color	Black	Dark gray to black	Reddish brown to black
Tenacity	Very brittle	Very brittle	Very brittle
Luster	Submetallic to metallic	Submetallic to metallic	Submetallic to adamantine
Fracture	Uneven	Uneven	Uneven
Hardness	5	5–5.5	5
Magnetism	Sometimes feebly magnetic	Slightly magnetic	
Streak	Dark brown	Dark brown	Brownish red to greenish yellow
Diaphaneity	Opaque to weakly translucent in cleavage plates	Opaque	Opaque to translucent
Common form of occurrence	Well-defined crystals, massive cryptocrystalline	Irregular masses, radiating groups of bladed crystals	Radiating groups of thin-bladed crystals

Some other minerals that may be considered in this group, but which are economically unimportant as ores of tungsten, are:

Wolframite crystal (Bolivia). 1⅓ times original size.
From authors' collection.

Reinite ($FeWO_4$): May be regarded as nearly pure ferberite, pseudomorphic after scheelite. Crystallization, tetragonal. Typical occurrence, Kimbosan, Kai (Japan).

Ferritungstite ($Fe_2O_3 \cdot WO_3 \cdot 6H_2O$): An oxidation product of wolframite. It is light yellow in color, much paler than tungstite, and is seen under a microscope to consist of hexagonal plates.



Crystallized ferberite from Nugget Mine, Gilpin County, Colorado. Natural size.

Tungstite or Tungsten ochre ($WO_3 \cdot H_2O$ or H_2WO_4): Also an oxidation product of wolframite and scheelite. It is yellowish in color, from pale to orange. Essentially it is anhydrous, although a rare form found in British Columbia, $WO_3 \cdot H_2O$, is apparently hydrous. It may be pointed out here that, as an ore, it has been found in some considerable quantity only at Easly and Juslee, east of La Paz, Bolivia.

Meymacite: As described by Carnot, may according to T. L. Walker, be the same as tungstite.

Thorotungstite [$2WO_3 \cdot H_2O + (ThO_2, CeO_2, ZrO_2) H_2O$]: An alteration product of scheelite and wolframite, found in the Malayan tin deposits. It is a dark, honey-yellow mineral.

Hydrotungstite ($H_2WO_4 \cdot H_2O$): Suggested by Paul F. Kerr as the name for a hydrous oxide of tungsten resulting from the oxidation of ferberite. It occurs in minute green tabular crystals. Occurrence, Oruro, Bolivia.

Limonite[56] [$(Fe_2O_3)_n\ WO_3\ (H_2O)_n$]: "This hydrous ferric oxide carrying tungsten has been found in considerable quantity at Galconda, Nevada. The tungsten is either absorbed as an intimate part of the limonite or present as tungstic acid in too fine a state of division to be distinguished."

Russellite ($BiO_3 \cdot WO_3$): Tetragonal. Color pale yellow to greenish. Hardness 3.5. Specific gravity 7.35 ± 0.02. It is an alteration product of native bismuth and wolframite.

Tungomelane: A new name proposed by Prof. P. F. Kerr for the tungsten-bearing psilomelane found at Golconda, Nevada. Analyses show that the material consists essentially of manganese, barium, potassium, and tungsten oxides, with water. The tungsten content of the Golconda material varies from about 1 to 7 per cent in terms of WO_3.

(2) The scheelite group contains only one economically important mineral, **scheelite:**

Composition	$CaWO_4$
Crystallization	Tetragonal
WO_3 and W (%)	80.6; 63.9
Cleavage	Good in 4 directions
Specific gravity	5.4–6.1
Color	Pale yellow, brown, commonly white
Tenacity	Very brittle
Luster	Vitreous to resinous
Fracture	Uneven
Hardness	4.5–5
Magnetism	Non-magnetic
Streak	White
Diaphaneity	Transparent to translucent
Common form of occurrence	Massive and in small grains. Scheelite exists sometimes as pseudomorph after wolframite

Fluorescence for the detection of scheelite.[51], [52], [53], [53a] It has been known that scheelite fluoresces a bright blue in the dark under the action of ultraviolet light. The application of this fact has led to the discovery of some important scheelite deposits in the field. When invisible ultraviolet rays strike a mineral, it causes a displacement of an outer electron in the atom. This displacement releases an emission of fluorescent light having a greater wave-length than the incident ultraviolet ray. In the case of pure scheelite the fluorescence is blue. However, the presence of molybdenum in scheelite modifies the fluorescence color, changing it progressively from pale blue to white, cream, pale yellow and chrome yellow as the content of molybdenum increases and when finally the transition from fine scheelite, $CaWO_4$, to powellite, $CaMoO_4$, is complete, the fluorescence appears flesh-colored. According to R. S. Cannon and K. J. Murata, scheelite that fluoresces white contains molybdenum roughly from 0.35 to 1.00 per cent and scheelite that fluoresces distinctly yellow contains more than 1 per cent of molybdenum.

Generation of ultraviolet rays may be effected by passing an electric current through a quartz tube containing a combination of argon, helium and neon, to which a small drop of mercury is added.

In this group, the following unimportant minerals may be mentioned:

Powellite ($CaMoO_4$): Crystalline to massive. Cleavable in one direction. Color, yellowish. Luster, shiny. Hardness, 3.5. Specific gravity, 4.3. Fluoresces cream to yellow under short-wave ultraviolet light.

Stolzite and Raspite ($PbWO_4$): Lead tungstate exists in nature in two forms: the former, being tetragonal in crystallization, belongs to the scheelite type, and the latter is monoclinic. Color: gray, yellow, green, also red; specific gravity, 7.9 to 8.1. Typical occurrence: Zinnwald, Saxony (Stolzite); Broken Hill, New South Wales (Raspite).

√**Wulfenite** ($Pb\,Mo\,O_4$): Tetragonal. Color wax-yellow, passing into orange-yellow. Hardness, 2.75–3. Specific gravity 6.7–7.0.

Chillagite [$Pb(W, Mo)O_4$]: Considered as a mixture of stolzite and wulfenite, in which the ratio of Mo: W is 3:1. Color, straw yellow; specific gravity, 7.5; crystallization, tetragonal. Typical occurrence: Chillagoe, Queensland.

Cuproscheelite and Cuprotungstite [$(Ca, Cu)\,WO_4$]: Tetragonal. Olive green. The latter variety contains very little calcium and may have the composition $CuWO_4 \cdot 2H_2O$ or $WO_3 \cdot 2CuO \cdot H_2O$ It has a bright yellowish-greenish color. Apparently it is a secondary mineral formed by the weathering of copper sulfide to copper sulfate, which in turn alters the scheelite to cuprotungstite. Typical occurrence: Kern County, California.

Tungstenite (WS_2): Earthy or foliated. Color and streak dark lead-gray. Hardness, 2.5. Specific gravity, 7.4.

Hollandite: Essentially a barium manganate containing variable amounts of WO_3 and ferric iron. Silvery gray to dark bluish or black. Hardness, 4.5 to 6. Specific gravity, 4.7 to 5.0. Analyses of pure mineral have shown as much as 0.63 per cent WO_3.

Minerals Containing Insignificant Amounts of Tungsten[56]

Tungomelane (variety of psilomelane or cryptomelane) $Mn_2O_3 + BaO + WO_3 + H_2O$.
Yttrotantalite, Hjelmite, Samarskite.
Microlite, Hatchettolite, Columbite, Tantalite, Schetelgite.
Sipylite, Germanite, Yttrocrasite.

Doubtful Minerals[56]

Alkinite, pseudomorph of wolframite after scheelite.
Calcioscheelite, synonym of scheelite.
Magnesioscheelite, hypothetical.
Tammite, possibly an artificial alloy.
Trimontite, a mineral proved to be scheelite.

Prof. Paul F. Kerr,[56] in the discussion of the tetragonal tungstate minerals, distinguished two groups:

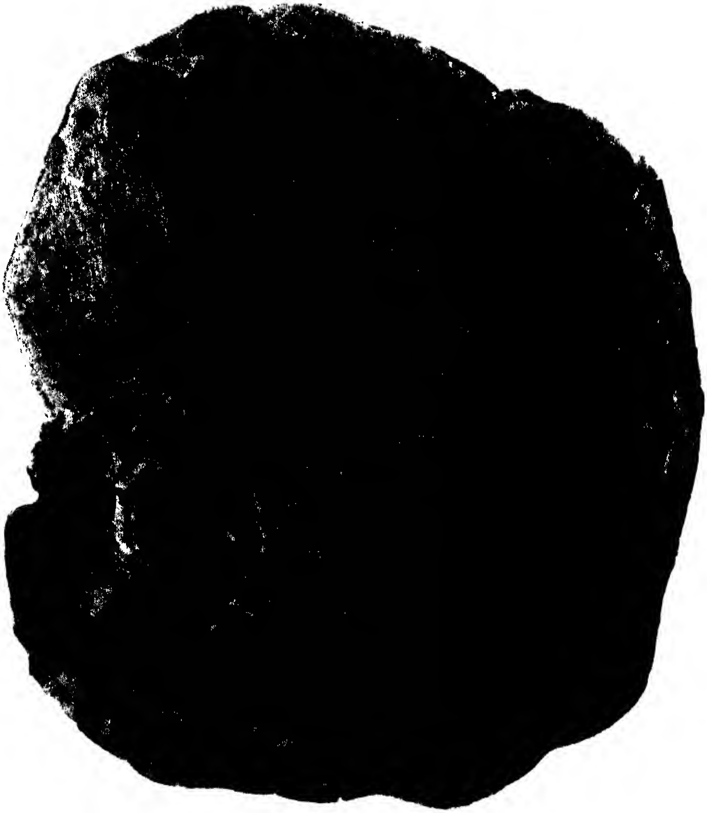
1. Scheelite-Powellite Group, with Seyrigite as an intermediate member of the group.
2. Stolzite-Wulfenite Group, with Chillagite as an intermediate member of the group.

"The isomorphism of the scheelite-powellite group and of stolzite with wulfenite is well established. Mineralogically these are considered as two separate groups—a calcium tungstate-molybdate group and a lead tungstate-molybdate group. . . . Scheelite which contains molybdenum and powellite which contains tungsten are fairly common." As to the second group, the minerals stolzite and wulfenite probably vary with chemical composition corresponding to the minerals of the first group.

Of the various tungsten-bearing minerals described above, only six—scheelite, ferberite, hübnerite, wolframite, and to a small extent cuprotungstite and tungstite—are considered to be ore-forming. The most important of these six minerals are wolframite and scheelite.

Genesis of Tungsten Ores

It is a truism to say that ore solution is a highly specialized form of igneous magma. (We are concerned here only with granite magma, as the parent magma from which tungsten ores originate.) When igneous magma intrudes into the surrounding rocks, differentiation and segregation within the magma proceed forthwith, giving rise, although slowly with the prog-



Above: Scheelite from Clifton mining district, Deep Creek Mountains, Tooele County, Utah.

Below: Scheelite and gray quartz from Kimberly-Montana Mine, Jardine, Montana.

From "Tungsten Minerals and Deposits" by Frank L. Hess, U. S. Geological Survey, Bull. 652, 1917.

ress of time, to the formation of ore deposits. We know that the temperature gradient of the granite magma gradually lowers as it ascends toward the surface. First the lime silicates are differentiated and solidify out; then silica (long-continued and overlapping) and iron oxide; and finally ores of molybdenite, cassiterite, wolframite, pyrite, arsenopyrite, sphalerite, chalcopyrite, galena, lead and silver sulfantimonides, etc. The so-called zonal theory, so well developed by Emmons, seeks to explain the above arrangement of minerals in ore deposits with reference to the parent igneous rock. Naturally we expect the superpegmatitic magmas to be the most prolific mother of most of the vein deposits. We may also imagine that "the rest-magma, in granitic rock, is a solution rich in alkalies and silica, probably with water, and may be pressed out of the partly consolidated magma as if from a sponge and crystallize as pegmatite",[3] and that finally, with lowering of temperatures, the granite juice, as it were, differentiates and solidifies last as ores, "in fissures held open by hydrostatic pressure of the fluids".

We shall now confine our attention to tungsten ore and incidentally tin ore, both being homogenetic and often closely associated in nature.

The volatile substances, which formed an integral part of the progressively acidic residual granite, consist of water and compounds of boron, fluorine, and chlorine, forming what are called mineralizers. These mineralizers, together with the acidic solutions, acted as powerful fluxes and as carriers for the deposition of wolfram, cassiterite, molybdenite, bismuthinite, pyrite, and arsenopyrite as found in the lodes in China, Burma, and elsewhere.

The water present was undoubtedly juvenile but existed also as hydroxyl in combination with silica and with some other minerals. When it is observed that there is a paucity of such mineralizers in a deposit, as happens in Tavoy, sulfides may be regarded, according to Jones[4], as "having played a most important part as carriers of wolfram and tin ore". The silica so universally prevalent as quartz in wolfram-tin veins or pegmatites is believed to have existed in a colloidal condition.

However, Prof. Paul F. Kerr[56] believed that "tungsten in solution exhibits an affinity for silicon, and probably within the magma the tungsten is in solution as some salt of silicic acid."

From the granitic magma up to the development of wolfram vein deposits, the following steps can be discerned: With decreasing temperature, the hot igneous melt would change to an aqueous igneous rest-magma from which pegmatites formed; then finally from the aqueous solution, that is, the wolfram-forming juice, veins developed. There is thus observed a gradation, however obscure sometimes, from magmatic differentiation to vein-forming; and it would not be incorrect so say that the mineralized veins containing the principal tungsten ores are generally of pegmatitic origin.

There are two rival theories to account for the development of vein formation: the hydatogenic theory, stressing the adequacy of aqueous solution, and the pneumatogenic theory, that of gas. In order to account for the origin of wolframite and its associated minerals in the veins in Tavoy, Dr. Morrow Campbell implicitly advocated the former theory, but it is unfortunate that he considered the water involved to be of meteoric derivation, rather than of magmatic origin, as is the case. Writing on the same matter, and leaning toward the pneumatogenic theory, Dr. William R. Jones on the other hand emphasized the importance of mineralizers in the development of wolframite and its associated minerals. Judging from the writings of Drs. J. Coggin Brown and A. M. Heron[5], it may be said that their opinion occupies the middle ground between these two views. There is no doubt that in Tavoy such pneumatolytic minerals as tourmaline, topaz, apatite, etc. are never, or at least very seldom, found in association with wolframite, although at Mawchi, tourmaline is found in the granite rock probably increasing in depth there. On the contrary, in the world-famous wolframite deposits in southern Kiangsi, China, such mineralizers as apatite, fluorite, tourmaline, and occasionally topaz are quite common as gangue minerals in the wolfram veins. Here it is conceivable that pneumatolysis has played a part in the development of such deposits. Again, the very common occurrence in Kiangsi and in Tavoy of greisen bands bordering veins in granite in which are found wolfram or cassiterite, or both, indicates the action of mineralizers. Thus, both hydrothermasis and pneumatolysis can be invoked to explain the genesis of wolfram and tin ore in deposits of both the vein and pegmatite type, with emphasis, however, on the former.

With respect to the origin of the pyrometasomatic type of tungsten deposits, that is, the contact metamorphic scheelite deposits in the Great Basin region in California, Nevada, and northwestern Utah, the foregoing discussion is equally pertinent. Discussing the formation of these deposits from the magmatic solution, Frank L. Hess and Esper S. Larsen[6] write: "The chief work of the moving solutions was (1) to carry the heat from the magma into the adjoining rock and thus raise the temperature of the rocks adjacent to the passageway for the solution; (2) to receive material from the contact zone; (3) to carry mineral from the magma or adjacent rock to the contact bodies and there deposit it; and (4) to bring about a recrystallization and rearrangement of the materials in the contact zone."

Myasnikov shows that scheelite ($CaWO_4$) can be formed by the reaction of silicotungstic acid $H_8\,[Si\,(W_2O_7)_6]$ with calcium carbonate.[43]

Associated Minerals and Their Paragenesis

According to William R. Jones[7], a more or less complete list of the minerals which occur in association with cassiterite, wolframite, and scheelite in the different tin and tungsten fields of the world is given below: quartz, feldspars (orthoclase, microcline, albite), muscovite, lepidolite, biotite, tourmaline, fluorspar, topaz, pyrite, arsenopyrite, chalcopyrite, bismuth, bismuthinite, molybdenite, stannite, galena, sphalerite, ilmenite, beryl, corundum, and apatite; and occasionally the following minerals are known to occur in a few deposits: andalusite, autunite, barite, chalcocite, columbite, epidote, graphite, grossularite, heterosite, lithiophilite, lollingite, melanite, monosite, petalite, rutile, scorodite, titanoferrite, spinel, spodumene, struverite, triphylite, triplite, and zircon.

According to Brown and Heron[8], the paragenesis of the important minerals in the wolfram and tin ore deposits in Tavoy is as follows: "Molybdenite appears to have been the first ore mineral to be deposited, as it is often enclosed in wolfram, or intergrown with the mica at the edge of the veins. It was followed by wolfram, cassiterite, bismuth, bismuthinite, and then the majority of the sulfides like pyrite, chalcopyrite, arsenopyrite, pyrrhotite, galena, and sphalerite. Pyrite belongs to several stages of the crystallization processes and is not always confined to its place in the general order given above. Fluorite was probably one of the latest minerals to be formed. It is usually found in crystals coating other minerals. It should be pointed out that all these compounds do not occur in every vein; the sulfides of lead, bismuth, and zinc are rarely found". In the well-known deposits in southern Kiangsi, the following associated ore minerals and gangue minerals are noted in association with wolfram and tin ores in the order of decreasing frequency of occurrence. Associated ore minerals: pyrite, bismuthinite, bismutite, arsenopyrite, molybdenite, bismuthospherite, scheelite, chalcopyrite, galena, sphalerite, chalcocite, bornite, pyrrhotite, psilomelane. Gangue minerals: quartz, muscovite, fluorite, feldspar, chlorite, sericite, lepidolite, topaz, tourmaline, chalcedony. Other less common minerals are: stannite, tetrahedrite, calcite, scorodite, smithsonite, malachite, azurite, marcasite, chalcocite, covellite, and beryl. Most of the veins contain both wolframite and a small percentage of cassiterite; however, there are veins in which cassiterite is absent. Perhaps the paragenesis of the minerals here is the same as that of the minerals found in the wolfram and tin ore deposits in Tavoy.

According to Hess and Larsen[9], "the chief minerals of the contact-metamorphic scheelite deposits are different from those of most other mineral deposits, comprising the silicates, garnet, diopside, epidote, vesuvianite, and hornblende. Quartz, calcite, and both potash and magnesian veins are common; and pyrite, chalcopyrite, pyrrhotite, molybdenite, sphalerite, magnetite, hematite, fluorite, zeolites, and a large number of other minerals are present in some deposits." The word "tactite" was coined by Hess to designate the dark silicates noted above.

In continuation of the discussion of the paragenesis of minerals, attention is now drawn to the controversy between William R. Jones[10] and J. Morrow Campbell[11] as to whether wolfram was deposited at a temperature lower than tin ore, or *vice versa.* The former maintained that cassiterite was deposited at a higher temperature before wolfram, which was deposited later at a lower temperature, while the latter maintained that wolfram antedated cassiterite. J. Coggin Brown, in his contributed remarks on Jones' paper, writes, "I am convinced that in the great majority of cases the wolfram is older than the tin ore. Dr. A. M. Heron has arrived at the same conclusion independently. At the same time there is no doubt that *cassiterite is present in relatively larger quantities in veins traversing granite than in those which pierce sedimentary rocks.** This apparent anomaly seems to suggest that temperature alone is not the deciding factor in the case." In his paper on the geology and ore deposits of the Tavoy district[12], he reiterates the same view: "As a general rule we find that cassiterite is present in relatively larger amounts in veins traversing the granite, than in others which pierce sedimentary rocks." This view of Brown can be corroborated from the various observations made on the occurrence of wolfram deposits in southern Kiangsi. Here, in a general way, tin ore is quite spare or entirely absent in veins found in the overlying sedimentaries, while those traversing the granite contain cassiterite in relatively large amounts. A typical instance is found in the deposit at Shenhengkow, Tayu, where the associated cassiterite occurs sparingly in the veins found in the overlying sedimentaries, but increases predominantly in the same veins traversing the granite below. According to Kechin Hsu, in the Tayu deposits the crystallization periods of wolframite and cassiterite overlap. "At places cassiterite lines the wall with the wolframite filling the central spaces; at other places, the reverse is true. At Hungshuichai, wolframite crystals are replaced by massive cassiterite along its cleavages and fractures." H. L. Haag[46] in his paper on Wolfram in Nigeria, makes this observation: "It is therefore submitted that we can safely say that outside the Younger Granite contact wolfram tends to occur without cassiterite or with almost negligible quantities; within the granite intrusion but near the contact a higher proportion of cassiterite tends to occur with the wolfram; although the latter is in several cases still found alone. Further within the intrusion cassiterite predominates . . . the wolfram and cassiterite zones clearly overlap to a high degree, but

---

* Our italics.

Large, imperfect crystals of wolframite, embedded in quartz and chalcopyrite. Natural size. From Cornwall, England.

From "Tungsten Minerals and Deposits" by Frank L. Hess, U. S. Geological Survey, Bull. 652, 1917.

the wolfram zone passes outwards from the granite contact somewhat beyond that of the cassiterite." Malcolm Maclaren[47] in his investigation of the wolfram deposit in Cornwall found that wolfram predominated in the zone between 840 and 1,200 feet from the surface while below 1,200 to well over 2,000 feet from the surface cassiterite prevailed. J. A. Dunn[48], from a study of this problem, came to this conclusion: Wolfram was probably the first mineral to form, but when cassiterite had started to form it developed much more rapidly, so that the ratio of Sn to WO_3 increased; then gradually and further from its source, wolfram increased in development to a position at which the ratio of Sn to WO_3 was at its lowest. In short, we may say that within a narrow range wolframite might deposit before cassiterite, or that the temperatures of formation of the two minerals might overlap; over a wide range, however, cassiterite would deposit before wolframite, that is, cassiterite is a higher-temperature mineral than wolframite. However, at present, we can say only that "this apparent anomaly seems to suggest that temperature alone is not the deciding factor" and that the controlling factors are pressure and relative saturation. The practical bearing of this discussion will be seen later.

Writing on tungsten deposits[13], Scrivenor quotes A. A. Henggeler thus: "Practically all our wolfram-tin ore comes from places where there is a contact of granite and schist. The quartz veins where traversing schist contain fairly pure wolfram. On the contact of granite and schist, the same veins carry mixed ore, and if they continue into granite, they get richer in tin and poorer in wolfram."

Decomposition of Wolframite and Scheelite in Nature

R. W. Gannett[14] obtained the following results from his experiments on the decomposition of scheelite, ferberite, wolframite and hübnerite with various solutions, such as are probably found in ground water:

"1. Carbonate solutions had no apparent effect on any of the tungsten minerals.

"2. Alkali hydroxide solution had no effect on scheelite, but dissolved tungsten from the wolframite.

"3. Salts of lime and soda, in the absence of acids, had no apparent effect.

"4. Sulfuric acid alone, and in combination with sulfates of lime, soda, manganese, and ferrous iron, dissolved portions of all the minerals.

"5. Hydrochloric acid alone, and in combination with chlorides of lime, soda, and manganese, had a solvent effect on the minerals.

"6. Manganous salts invariably gave increased solution.

"7. Ferric salt in most cases seemed to inhibit any reaction, but in the case of scheelite the reaction is not completely stopped, although it is reduced to small proportions. In the case of ferric chloride, the acid present did not prevent hydrolysis, so the active solution contained no ferric chloride, but was instead faintly acid, and so had a solvent action.

"8. Sulfate solutions are more active than chloride solution.

"9. Manganous solutions and possibly ferrous solutions brought about an interchange of lime from the scheelite with the manganese, and possibly with iron of the solution.

"10. The more active solutions left an H_2WO_4 precipitate in the test-tubes with scheelite.

"11. Except by sodium hydroxide, scheelite is more readily attacked than ferberite or wolframite.

"12. Humic acids are inactive.

"13. Wolframite and ferberite, while giving the same general results, are attacked in different degrees by different solutions."

Some of the preceding laboratory results may seem to find confirmation from observations in the field. On the other hand, J. Morrow Campbell[15] observed that alkaline carbonates in solution in unoxygenated, carbonated water have in nature a decided solvent action on wolfram, and that when wolfram is exposed to the action of oxygenated water, the acid radical is leached, with the result that a residue of ferric and manganese hydrates is left behind. The product of the decomposition of wolfram and scheelite in nature may be thus summarized, according to Campbell:

1. Wolfram may be removed from an alluvial by comminution or by solution, or by both combined.

2. Sulfuric acid, resulting from the action of oxygenated water on pyrite, attacks tungstates, but scheelite before wolfram; calcium sulfate results in the former case, and ferrous and manganous sulfates in the latter, all of which are soluble in water, the last two being oxidized with precipitation of the hydrates on adjacent solids, often as glassy black coating.

3. Hydrated tungstic oxide, when derived from wolframite, remains behind as a yellow powder.

4. Decomposition of scheelite takes place with comparative rapidity along cleavage places and cracks, resulting in the formation of tungstic hydrate, which, however, is readily dissolved by alkaline carbonates in ground water.

5. Secondary scheelite probably results from the action of calcium sulfate solution on alkaline tungstate in an excess of alkaline carbonate solution.

According to P. F. Kerr,[44]: "Specimen of wolframite or scheelite may be altered to an ocherous colloidal product containing both tungsten and iron. Such a product has been observed in specimens of scheelite or wolframite

Above: Hübnerite from Birdie Mine, Butte, Montana.
* *Below:* Hübnerite from Gladstone, near Silverton, Colorado.
From "Tungsten Minerals and Deposits" by Frank L. Hess, U. S. Geological Survey, Bull. 652, 1917.

from Lane's Mine, Long Hill, Connecticut; Meymac, France; Lead, South Dakota; and San Casmado, Portugal."

Secondary Enrichment

Secondary enrichment of tungsten deposits of any economic importance is not known to exist. This view is thus summarized by Gannett: "In some deposits, associated minerals other than those containing tungsten dissolve more readily than tungsten minerals, and there is enrichment near the surface by removal of valueless material. Tungsten minerals, nevertheless, dissolve rather readily, and form soluble salts or colloidal compounds that may remove the tungsten from the outcrop. The tungsten may be leached from its ore bodies without being redeposited below. The facility with which tungsten compounds in solution will hydrolyze and form insoluble compounds tends to prevent downward immigration of tungsten, and there are probably no extensive zones of tungsten minerals like those of copper and silver, although enrichment by solution and reprecipitation probably does occur to a small extent. Ferric sulfate, which increased the solution of copper and silver, slows down or stops the solution and immigration of tungsten.

From the foregoing discussion it can readily be concluded that typical alluvial deposits of tungsten are not to be found. The so-called alluvial deposits are in fact either detrital deposits of hill slopes or residual desert deposits. These may also be called eluvial deposits. The so-called placer deposit of scheelite at Atolia, California, may be only a residual desert deposit and is not an alluvial deposit in the true sense of the term.

II. CLASSIFICATION OF TUNGSTEN DEPOSITS

Tungsten deposits can be classified or grouped according to their genesis, mineragenetic epochs, and metallogenic provinces.

I. Genetic Classification

Following the genetic classification of mineral deposits by Lindgren, tungsten deposits can be classified into six groups: (1) Orthotectic, (2) Pyrometasomatic, (3) Hypothermal, (4) Mesothermal, (5) Epithermal, (6) Surface.

Under orthotectic (this term is adopted from Graton and McLaughlin[16]), whose temperature of formation is 575–1000°, there are two zones of formation; the lower limit is represented by pegmatoid deposits, such as occur in Burma, China, the United States and elsewhere, and the upper limit by segregation deposits (dissemination deposits), such as those found in the granite at Mawchi, Burma. The latter form of deposit is of only theoretical interest, as no valuable deposit of such type has ever been found.

Under pyro-metasomatic, whose temperature of formation is 500–800°, are the so-called contact metamorphic deposits, such as the scheelite deposits in California and Utah. According to Frank L. Hess, "few tactite tungsten deposits (contact metamorphic deposits) are known outside of the United States, though they are found on King Island, between Tasmania and Australia, in Mexico, and Korea".*

Under hypothermal, whose temperature of formation is 300–500°, are the quartz vein deposits. Most of the tungsten deposits of the world are of the vein type. The gangue is commonly quartz, although calcite in greater or less quantity is prevalent in scheelite-bearing veins. Pyrite is another mineral that is quite common in tungsten-bearing veins. Arsenopyrite and chalcopyrite are generally found in wolframite veins, but to a less extent in scheelite veins. Molybdenite and bismuthinite occur in most wolframite veins in the Sino-Malaysian Province, though they rarely occur in such association in the United States. Galena, zincblende, stibnite and cinnabar are found sparingly in tungsten veins. It would seem that, judging from the great amount of cassiterite combined with the wolframite and from the associated minerals present, the Chinese, Malayan and Burmese tungsten deposits might have been formed at higher temperatures than those in Bolivia, Portugal and Australia. Generally speaking, the quartz veins in granite were formed at higher temperature than those found in the overlying sedimentaries. Most of the tungsten deposits of the world belong to this class.

From the common presence of fluorite and sericite in the quartz veins and the persistency in the parallelism of their strikes, some Kiangsi deposits may be considered to belong to the mesothermal zone of formation (200–300°). Also Lindgren considered the tungsten deposits of Boulder County, Colorado, as belonging to this class.

Epithermal deposits of tungsten (50–200°) are rare. Perhaps the hübnerite veins in Tonopah, Nevada and Cripple Creek, Colorado, are of this type.

Eluvial deposits are common in certain regions in China and Burma, but are becoming of less importance. However, the placer deposits of scheelite at Atolia, California, may still be of importance. Tungsten minerals are resistant to solution and oxidation; yet, being friable, they are easily pulverized by running streams, and in this condition they are changed to the more soluble hydrous oxide form and are thus washed away.

Attention must be drawn to the fact that the zones of formation, as described above, have no distinct boundaries, but grade one into another and even overlap. An unusual composite type of deposit is the scheelite

---

* Mention should be made here of the extensive contactic metamorphic deposits of tungsten, discovered recently in Brazil.

deposit of the Reaper Mine in Utah. It is a pneumatolytic-tactite-pegmatite-vein-dike, where the different zones of formation completely overlap.[42] Another unusual deposit is the manganese oxide and tungsten deposits of Golconda, Nevada, which may be classified as a type intermediate between the surface and epithermal zones of formation.

From the standpoint of genetic classification of tungsten deposits, the term "Replacement Deposit" is not used here on account of its indefiniteness. Replacement deposits may be formed after hypothermal, mesothermal, or epithermal veins or pegmatitic veins, when the vein-making solutions attack such easily soluble rocks as limestone or dolomite. We may consider greisen, if it contains tungsten minerals, as replacement deposits.

Temperature of Formation	Zones of Formation	Subzones	Forms		Examples
Atmospheric	Surface		Eluvial		Placer deposit of scheelite at Atolia, California
50–200°C	Epithermal		Quartz vein	Replacement Deposits	Hübnerite veins in Tonopah, Nevada, and Cripple Creek, Col.
200–300°C	Mesothermal		Quartz vein deposits		Boulder County, Col.
					Kiangsi deposits, Chinese
300–500°C	Hypothermal	Lower limit	Quartz vein deposits		Kiangsi deposits, Chinese Bolivia deposits Portugal deposits Australia deposits
		Upper limit	Quartz vein deposits		Malay deposits Burma deposits Kiangsi deposits
100–800°C	Pyro-metasomatic		Contact metamorphic deposits		Scheelite deposits in California, Utah
575–1000°C	Orthotectic	Lower limit	Pegmatoid deposits		Pegmatites in Burma, China, U. S.
		Upper limit	Segregation deposits (Dissemination deposits)		Granite, at Mawchi, Burma

II. Metallogenic Provinces

Grouped in metallogenic provinces, the tungsten-bearing areas of the world are as follows, in the order of their economic importance:

	Magnitude of Production, % (1913-1937)
1. The Sino-Malaysian Province	62.6

A. China Subprovince:

(a) Nanling Region (Including southern Kiangsi, southeastern Hunan, northern Kwangtung); Kiangsi (17 districts, 80 mining localities)

Important producing centers:

Siao Lung
Pan Ku Shan
Hung Shui Chai
Si Hua Shan
Shang Ping
Ta Chi Shan
Kuei Mei Shan

Hunan (9 districts, 12 mining localities);

Important producing centers:

Lo Chang Ping
King Chuan Tong
Lei Tze Ling
Yao Kang Hsien
Wu King Ping
Tze Hsing
Yu Chen

Kwangtung (36 districts); important producing centers:

Wen Yuan
Hoi Fung
Yo Chang
Mei Hsien
Chung Shan
Ho Yuan

(b) Kwangsi Region; important producing centers:

Bing Yang
Hwai Chi
Kung Shing
Fu Chuen
Sin To
Ho Hsien
Teng Hsien

(c) Yunnan: Mengtze Region

B. Burma Subprovince:

(a) Mawchi Region (b) Tavoy Region (c) Mergui Region

C. Malaya Subprovince

D. Siam Subprovince

E. Indo-China Subprovince

2. North American Cordilleran Province* (13 states)	10.8

---

* The admirable memoir[56] on "Tungsten Mineralization in the United States" by Prof. Paul F. Kerr came to the notice of the authors only after the manuscript was in the hands of the publisher. His classification of the Cordilleran tungsten

A. The Great Basin Subprovince:
- (a) California-Nevada Belt Region
- (b) Utah Region
- (c) Arizona Region
- (d) Oregon Region

deposits is more logical than that of the authors. His classification, with brief descriptions, is as follows: (vide map, p. 61)

1. *Eastern Arc*

"The eastern arc follows a line of Tertiary igneous intrusives extending northeasterly from the Colorado plateau, and southerly into New Mexico. The extension of the arc across Wyoming and into Montana is indefinite.

"A characteristic of the region is the occurrence of tungsten minerals in quartz veins, or quartz replacements, and in general the absence of typical contact-metamorphic deposits. The predominant tungsten minerals are members of the wolframite group, while scheelite is found in minor amounts. At San Juan, Colorado, the chief tungsten mineral is huebnerite; ferberite predominates in the Boulder district, and wolframite in the Black Hills. Scheelite occurs in Wyoming. In Colorado the intrusives probably related to the tungsten mineralization are Tertiary. Tertiary tungsten mineralization has also been described in the Black Hills, although many of the occurrences there are presumably pre-Cambrian.

2. *Central Arc*

"This arc crosses New Mexico, Arizona, California, Nevada, Utah, Idaho, and Montana. In the Dragoon Mountains in southeastern Arizona at Las Guijus south of Tucson near the Mexican border, and at Boriana just east of Needles, California, quartz veins have yielded considerable quantities of wolframite, scheelite, or huebnerite. Minor occurrences have been reported from a number of intermediate localities. Manganese-bearing deposits in this region are known in a number of instances to carry tungsten.

"The central arc continues northward from Arizona along the eastern margin of Nevada, extending well into Utah, and continuing until all evidence of mineralization is concealed by the lava fields of southern Idaho. The outstanding localities in the eastern part of Nevada lie in the Snake Range. The Minerva, Hub, Osceola, and Tungstonia districts have a fair record of past production. Both scheelite and huebernite are prominent in this region. To the northwest at Bald Mountain and in the Ruby Range scheelite is a contact-metamorphic mineral. In the Snake Range, although scheelite as found at Minerva and near Osceola occurs in limestone or in calcareous sediments, it appears to be closely related to the formation of quartz veins and lacks the typical characteristics of the contact metamorphic deposits of western Nevada. A number of the deposits in the Milford district and elsewhere in Utah are contact-metamorphic in type but differ somewhat from the western deposits.

"The central arc continues east of the Idaho batholith and appears to trend toward the Boulder batholith. The chief tungsten locality in eastern Idaho is the Ima mine in the Lemhi range east of the Salmon River and just south of the Montana boundary. Both scheelite and huebnerite are found in this region. Huebnerite, however, is the principal mineral mined. Contact-metamorphic deposits are well known as at Mackay, Idaho, but scheelite is apparently a minor constituent in contact zones. Deposits appear to be chiefly of the quartz-vein type. In eastern Washington and the panhandle of Idaho the central arc and the Western arc seem to merge into a single broad belt that continues northward through British Columbia.

"The tungsten occurrences of this region are all either within or near acidic igneous intrusives. Some scheelite has been found, even in commercial quantities as at Boriana, and traces of contact-metamorphic scheelite have been reported at Johnson, Arizona, in the Dragoon district, but most of the deposits are of the quartz-vein type.

3. *Western Arc*

"The western arc, economically the most productive, extends from southern California into eastern Oregon, Idaho, and Washington.

"Outstanding producing areas in California have been Atolia, Posey, Tungsten Hills, and Pine Creek. Among localities in Nevada economically important have been Silver Dyke, Nightingale, Oreana, and Mill City. The Yellow Pine deposit

- B. The Rocky Mountain Subprovince:
    - (a) Boulder County, Colorado Region
    - (b) Idaho Region
    - (c) Montana Region
    - (d) Washington Region
    - (e) New Mexico Region
    - (f) South Dakota Region
- C. Alaska
- D. Mexico

3. The Andean Province: 9.0
    - A. Bolivia Subprovince:
        - (a) La Paz Region
        - (b) Cochabamba Region
        - (c) Oruro Region
        - (d) Potosi Region
    - B. Argentina Subprovince:
        - (a) San Luis
        - (b) Cordoba
        - (c) Catamarca
        - (d) San Juan
        - (e) Mendoza
    - C. Peru and Chile
4. Australian Province: 3.3
    - A. Eastern Australian Cordilleran Subprovince:
        - (a) Queensland
        - (b) New South Wales
        - (c) Victoria
        - (d) Tasmania
        - (e) New Zealand
    - B. Northern Territory and Western Australia Subprovince
5. Japan and Chosen Province 3.5
6. Iberian Peninsula and Cornwall Province: 6.7
    - A. Portugal Subprovince
    - B. Spain Subprovince
    - C. Cornwall Subprovince
7. Brazil
8. Other Regions:

    Africa, Cuba, Canada, Russia and other European countries.

It is obvious that there are many small producing regions that are, geologically speaking, outside the above-mentioned metallogenetic provinces. Quoting G. A. Roush[17]: "Tungsten ores are widely scattered over the earth and many other countries have shown minor outputs at various periods,

---

in Idaho lies along this line. Germania in Washington has been the principal producing deposit in the northern part of the arc.

"Tungsten mineralization is apparently related to post-Jurassic intrusives, and deposits are found either within or near areas of these intrusives. Scheelite, the prevailing mineral, has been found in commercial quantities both in contact-metamorphic deposits and in quartz veins. In a few localities huebnerite and wolframite occur, as for example at Germania, but these occurrences are minor compared to the occurrences of scheelite farther south.

"Tungsten of later origin is found in places along this belt. Psilomelane and limonitic ores containing substantial amounts of tungsten appear to represent concentrations of hot-spring origin and have been found along the east margin of the western arc as at Golconda and Sodaville, Nevada. The Golconda ores have been developed economically. Tertiary huebnerite has been reported from Alpine County, California."

particularly during the war, but the sum total of all of these during the period 1913–1937 was only 3.8 per cent of the total output. Among these countries, each of which contributed less than 1 per cent of the 1913–1937 total, are the following: Austria, Brazil, Canada, Chile, Czechoslovakia, *France*, *Germany*, Italy, *Mexico*, Netherlands East Indies, *New Zealand*, Nigeria, Norway, *Peru*, Rhodesia, Russia, South Africa, and Sweden. The five countries listed in italics furnished nearly three-quarters of the combined output, leaving only about 1 per cent to be supplied by the other thirteen."

It is significant to note that none of the metallogenetic provinces is situated in the interior of a continent and that all of them, except the Sino-Malaysian Province, border on oceans. It does not seem that this happened fortuitously; some fundamental reason must be sought[18]. "The coastal Cordilleras (the Rocky Mountains and the Sierra Nevada of North America, the Andes of South America, the Dividing Ranges of Australia, etc.) are located on the margins; the meeting places of the rising continental Cordilleras and the sinking suboceanic trough are the natural loci of the zones of special instability; . . . in order to maintain isostatic adjustment, the rock had to flow from under the ocean to bring more material into the column under the mountain areas, with great telluric pressure, which urged the rock magmas vertically upward, bringing with them the metallogenic minerals (tungsten minerals included) from the reservoir of the abyssal deeps, to form intrusions, either as batholiths, sills, dykes (pegmatites), or as veins according to the strength and character of the invaded rocks and the temperature and pressure controlling their differentiation and segregation. With regard to the Sino-Malaysian metallogenetic province, this reasoning may not be applicable. Perhaps the development of the extensive granite masses in southeastern China, Burma and Malaya, from which the tungsten deposits had their origin, might have some connection with the development of the arcuate chains in southeastern Asia.

III. Metallogenetic Epochs

It has already been shown that tungsten deposits are genetically related to igneous rocks of the acidic types. The intrusion of these igneous rocks took place during definite geological periods, following orogenetic disturbance. In studying the tungsten deposits of the world, we can divide them into those of:

1. Hercynian Age: Cornwall, Spain, Portugal, Australia (Permo-Carboniferous)
2. Late Mesozoic Age: Malaya, Burma, China, North American Cordillera
3. Tertiary Age: Andean Cordillera, North American Cordillera

CHINA

China leads the world as a tungsten producer. During the 25 years from 1913 to 1937, she contributed about 37 per cent of the world's production. About 95 per cent of the Chinese output comes from Kiangsi, Hunan and Kwangtung of which Kiangsi is by far the most important, contributing, as it does normally, 70 per cent of China's total production.

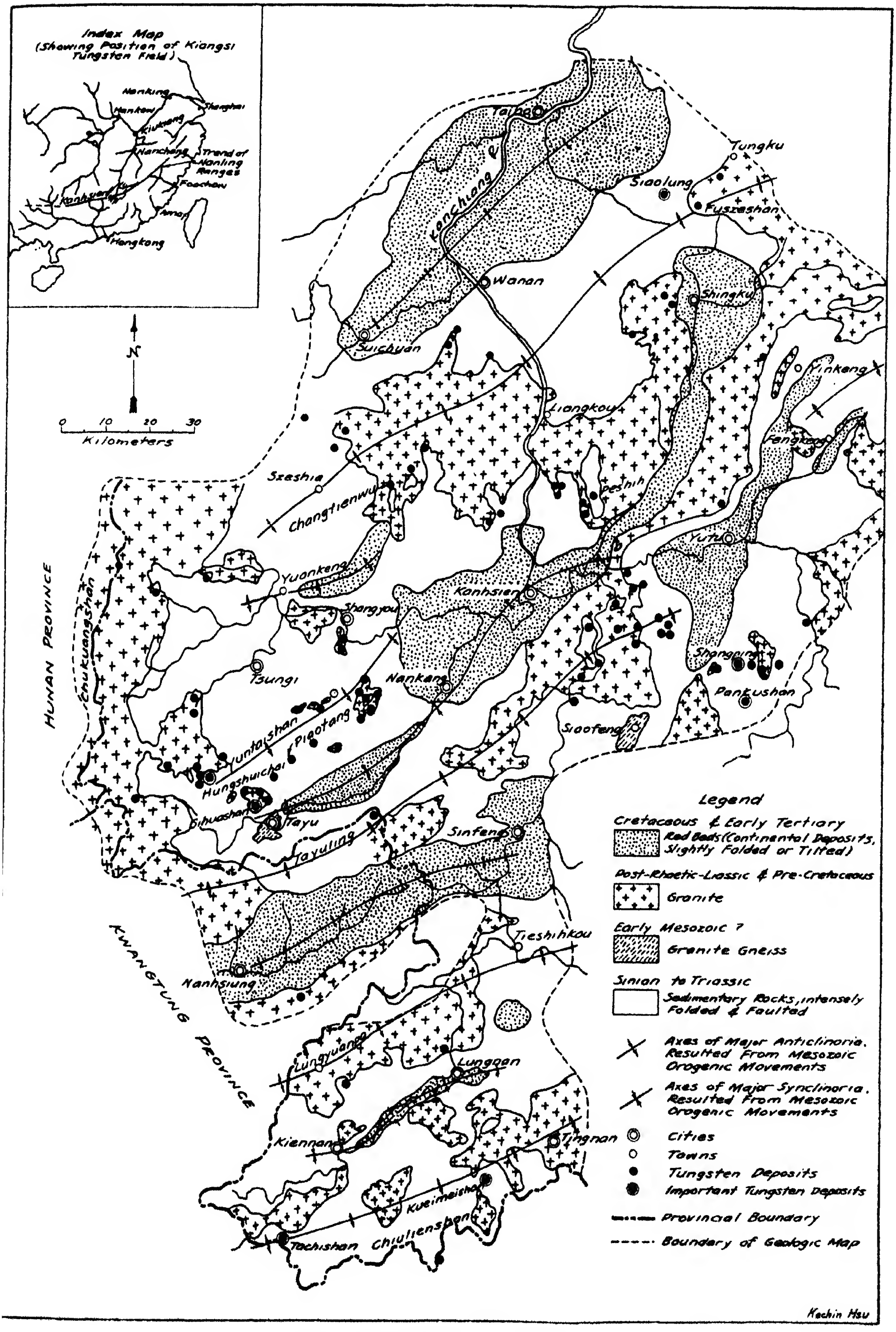
Kiangsi Province[19]

Practically all the tungsten deposits in China occur in what is commonly known as the Nanling region. It is a broad mountainous land, covering a vast area, including southeastern Yunnan, northern Kwangsi, northern Kwangtung, southern Hunan and southern Kiangsi. This mountainous region trends generally from ENE to NE and is roughly parallel to the sea-coast of southern China. Geologically this region is characterized by zones of intensely and complexly folded mountains, by wide-spread late-Mesozoic granite intrusions, and by rich high-temperature metallic deposits, containing tungsten, tin and some bismuth and molybdenum.

In general these parallel mountains follow the axes of different anticlinoria, along which the granite intrusions are now exposed. It is in these zones of intense folding and extensive granite intrusion during Mesozoic time that the rich tungsten deposits were formed.

Stratigraphy. The different geological formations recognized in this region are as follows:

Lower Pleistocene	Red Clay
Late Tertiary (Pliocene)	Kanhsien Gravel
	Unconformity
Early Tertiary (Eocene)	Yutu Red Beds
	Unconformity
Cretaceous	Loyao Red Beds
	Unconformity
	Intrusion of the Nanling granite, and formation of tungsten deposits
Triassic	Tieshikou Series
	Unconformity
Upper Permian	Loping Coap Series
	Unconformity
Middle Permian (Yangsinian)	Mingshan Formation Siaochiangpien Formation Chihsia Limestone
	Unconformity
Lower Permian (Uralian)	Chuanshan Limestone
Middle Carboniferous (Moscovian)	Huanglung Limestone
	Unconformity
Lower Carboniferous	Tseshui Coal Series Unconformity Changtungpei Series
Devonian	Shiashan Sandstone—Yuankeng Series
	Unconformity
Pre-Devonian (Silurian)	Tanchiapa Phyllites
Metamorphics (Siluro-Ordovician)	Tienmashan Series
(Sinian and Cambro Ordovician)	Fengkang Series



Map of Kiangsi tungsten field.

The numerous tungsten deposits in southern Kiangsi may be classified into several zones according to their genetic relation to the granite intrusions and the geologic structure. They are tabulated below from north to south: (map, p. 25)

Major structural units	Granite intrusions	Tungsten deposits
Taiho synclinorium		
Tungku-Szeshia anticlinorium	Batholiths	First zone
Yuankeng synclinorium		
Yuntaishan anticlinorium	Separate smaller intrusions	Second zone
Chikiang synclinorium		
Tayuling anticlinorium	Batholiths	Third zone
Sinfeng-Nanhsiung synclinorium		
Lungyuanpa anticlinorium	Batholiths	Fourth zone
Lungnan synclinorium		
Chiulienshan anticlinorium	Batholiths	Fifth zone

In southern Kiangsi, the predominant igneous rock is the Mesozoic granite to which the tungsten deposits are genetically related. Gneisses derived from granite were found at several places. Other Mesozoic intrusions in this region include diorite, quartz monzonite, granite porphyry, quartz porphyry, lamprophyre, aplite, and pegmatite. These occur mostly as dikes and other small irregular bodies. Cretaceous rhyolite and trachyte flows and volcanic tuffs, and Tertiary basalt porphyry were locally represented.

The Nanling Granite. In the entire Nanling region, the Mesozoic granite forms large batholiths, covering hundreds to thousands of square miles, together with stocks and cupolas of varying size. In southern Kiangsi the granite exposures cover about one-fifth of the total area surveyed. They are mainly in the broad cores of the Yenshanian anticlinoria. The geological map (p. 25) shows that in each of the five anticlinoria, there is a corresponding batholith. Some of these are continuously exposed for a hundred miles or more; others are partly covered by metamorphic rocks and are exposed as separate and disconnected intrusions.

Apophyses of pegmatite and aplite, as well as quartz veins, are common around the margin of the granite intrusions. The latter are rare toward the interior portions of the larger intrusive bodies. Certain lamprophyre and diorite dikes cut the granite in places.

The intense pneumatolysis of the granitic rocks is evidenced by the following facts:

1. The occurrence of tourmaline, fluorite and lithia-mica in the fresh granite.
2. Pegmatites and the tungsten-bearing quartz veins, associated with granite carrying abundant pneumatolytic minerals, such as tourmaline, lithia-micas, fluorite, topaz, and beryl.
3. Tourmaline not uncommonly found in argillaceous rocks at contact with the granite.

The granite gneiss occurs in a few localities: at Hsiafengshu, southeast of Kanhsien City; and around Tayu City, southwest of the Tingnan district. It is orthogneiss, derived through the metamorphism of granite intrusions.

Mode of Occurrence of the Deposits. Within an area of 14,000 square miles in southern Kiangsi, many tungsten deposits occur. More than eighty localities are now being worked. The deposits are not distributed at random, but in the main are restricted to the broad cores of the major anticlinal zones, which were formed in the Yenshanian period, and which trend generally ENE.

As stated, such deposits are closely associated with the granite intrusions, which, being related to the intense Yenshanian folding, were mainly localized in the broad axial portions of the major anticlinoria. Hence it is natural to find the tungsten deposits in these zones.

Most of the tungsten veins in southern Kiangsi were found either in granite or in sedimentary rocks near the granite contacts. Some of them occur near bosses of quartz monzonite, granite porphyry and diorite, and a few lie in sedimentary rocks far away from igneous exposures. Since veins of these groups are mineralogically identical with the veins associated with granite, and since they lie in belts marked by scattered granite cupolas, it is reasonable to suppose that there may be some granite bodies underlying these deposits. And it appears probable that all the tungsten deposits in this area are genetically related to the granite.

The general rule regardiug the occurrence of tungsten lodes is that they are located not far from the peripheries of granite intrusions. The top portions of intrusions are almost always most favorable for such deposits. In general, we may take the commonly dome-shaped contact of granite as an ideal surface of reference, which divides the tungsten lodes vertically into two groups of about equal value. In Kiangsi, it is common to find both sedimentary rocks and granite in one mining district. In such cases, almost all the tungsten lodes in granite can be traced upward or laterally to the contact, and some of them extend farther into the overlying sediments. Veins, which are chiefly in sediments, can commonly be traced downward or laterally to the granite contact or farther into the underlying granite.

As the degree of erosion and the shape of the intrusion differ from place to place, the granite is exposed in various sizes and shapes. According to their occurrence in different parts of granite intrusives, the tungsten deposits in southern Kiangsi can be classified as follows:

1. Deposits above, near, or in the granite stocks or cupolas (in granite or in sedimentary rocks).
2. Deposits in or below the roof-pendants of granite batholiths (in sedimentary rocks or in granite).

3. Deposits around the marginal parts of granite batholiths (in sedimentary rocks or in granite).
4. Deposits in the granite batholiths themselves, without sedimentary rocks nearby (in granite only).

Deposits of the first group are the richest and most numerous. Those of the second and third groups include a great many deposits, but many of them are not as rich as those of the first group. Deposits of the fourth group are rare and as a rule carry only low-grade ores. In the central portions of the great batholiths, there are no tungsten deposits nor even any barren quartz veins. Only at a few places at high altitude are there some very lean tungsten veins. Obviously then, the rich tungsten deposits are associated with smaller granite exposures rather than with larger ones, that is, top portions of granite intrusions are most favorable.

Statistically, there are more mining localities that produce ore from veins in granite than from veins in sedimentary rocks. But veins in sedimentary rocks as a whole yield 54 per cent, while those in granite produce only 46 per cent of the total output of tungsten ore from southern Kiangsi. Veins in sedimentary rock are, therefore, more productive than those in granite. Of course, grade of ore varies considerably with local conditions. For instance, with large, batholithic granite exposures, richer ore-bearing veins lie mostly in the sedimentary rocks above the granite, whereas with small granite exposures, like those in the Yuntaishan zone, veins in granite and in sediments are equally good. At Sihuashan and Hungshuichai of Tayu, small granite intrusions are overlaid concordantly by phyllite. Due to the impermeability of the phyllite covering, most of the tin-tungsten veins in the granite end abruptly against the phyllite contact. There the veins are quite rich immediately below the contact, probably due to the impounding of solutions by the cover rock.

Occurrence in Certain Geological Formations and Types of Country Rocks. As the granite is commonly in contact with pre-Devonian strata, most of the tungsten veins in sediments are in these pre-Devonian rocks. Only a few lie in Devonian sandstone. Upper Paleozoic and Triassic formations were invaded in places by granite, but no ore has been found in them. The country rocks of these tungsten veins are phyllite, sericitic sandstone, quartzite, argillite, graywacke, and quartzose mica schist. These are the common rocks of the pre-Devonian strata. They are cut by ore veins at various angles with regard to their bedding planes. The thick-bedded Permo-Carboniferous limestone is found in two mining localities, where it was metamorphosed by nearby granite intrusions. But no ore was found in the limestone.

Geographical Distribution

The geographical distribution of tungsten deposits in southern Kiangsi is represented on the geological map (p. 25). These deposits are grouped into the following five zones corresponding to the major structural units from north to south:

1st zone..........................From Tungku to Szeshia
2nd zone.........................Zone of Yuntaishan
3rd zone..........................From Tayuling to Shangping
4th zone..........................From Lungyuanpa to Shentushui
5th zone..........................Zone of Chiulienshan

The following brief outlines give a bird's eye view of these tungsten-producing araes:

First zone: This zone is some 70 miles long and 25 to 30 miles wide. Granite is exposed extensively, indicating a great batholith. The central portion of the batholith is practically barren. Around the marginal parts and in the roof-pendants there are scattered deposits, whose grade of ore is comparatively low, and whose total production is limited. But in the northeast end occur the rich deposits of the Sisolung district. Wolframite-quartz veins occur in sedimentary rocks when there are no igneous exposures nearby.

Second zone: The Yuntaishan zone is some 35 miles long and 12 miles wide. Within this zone occur many rich tungsten deposits which together produced, in 1937, 4000 metric tons of wolframite concentrates averaging 67 per cent of WO_3 and constituting nearly one-half of the total output of Kiangsi. Cassiterite is associated with tungsten ore in many deposits and is recovered as a by-product. The annual yield of cassiterite concentrates averaging 60 per cent tin is about 1500 metric tons. In all the other tungsten-producing areas of Kiangsi, outside of the Yuntaishan zone, there is not enough tinstone to justify its recovery. The leading mining camps of this zone are Sihuashan and Hungshuichai. The former yields chiefly tungsten and the latter yields more tin than tungsten. Within this zone, there are no large exposures of granite, but there are numerous small granite stocks with which rich tin-tungsten deposits are associated.

Third zone: In the western portion of this zone, south of Kanhsien, granite is as extensively exposed as in the first zone. Although many small deposits are being worked, their total annual production of wolframite concentrates is not more than 200 metric tons.

Further eastward to the south of Yutu, where a few granite cupolas are revealed below a thick covering of pre-Devonian and Devonian sediments, there occur several important bismuthinite-wolframite deposits. These deposits together yield annually about 1300 metric tons of wolframite concentrates averaging 72 per cent WO_3. The leading locality is Pankushan, which is one of the best deposits in Kiangsi. Bismuthinite and its weathering product, basic carbonate and oxide, found in the upper horizons of the veins, yield annually about 70 metric tons of concentrates averaging 65 per cent bismuth.

Fourth zone: This zone extends westward through part of Kiangsi into southern Sihsin district of northern Kwangtung (outside of the map) where many small tungsten deposits are mined. In Kiangsi there is no important mine in this zone, though several small deposits were discovered.

Fifth zone: The Chiulienshan is a continuous mountain range, 1,000–2,000 meters above sea level, trending ENE and forming the borderland between Kiangsi and Kwangtung provinces. This range is composed wholly of pre-Devonian sediments with a number of granite intrusions exposed in both the northern and the southern foothills. In the sedimentary rocks of this range, there are two important tungsten localities, Tachishan and Kweimeishan. Their production is large and their ores are of high grade.

Ore Bodies

Shape of ore bodies. The chief tungsten deposits in Kiangsi, as well as those of the whole Nanling region, are regular fissure-filling veins. They are well-defined tabular bodies with flat walls and unvarying strike and dip. The chief minerals are quartz, wolframite, and light-colored micas. Various other minerals occur locally.

At a few places, however, in addition to the regular veins, there are certain other types of ore bodies, such as:

(1) Irregular ore-bearing pegmatites;

(2) Irregular pneumatolytic replacements in granite and aplite, carrying cassiterite, and locally some wolframite, scheelite, and bismuthinite;

(3) Great lens-shaped wolframite-quartz bodies, in sedimentary rocks and in granite.

(4) Wolframite in quartz stringers and in sedimentary rocks.

These irregular ore bodies are comparatively rare and economically unimportant. They do not occur as single, isolated deposits but are associated with the fissure veins which are described below:

Width of veins. Tungsten veins range in width from paper-thin to 2–3 meters. Commonly they are 0.1–0.6 meter wide. Those more than a meter wide are called "wide veins". In many places, veins are so closely spaced that many of them may occur within four or five feet and may be mined by one drift. In such cases, even the minute veins are workable.

Lateral and vertical variation in the width of veins is common, but usually the wider veins, after running for a long distance, still maintain their great width. Branching and anastomosing of nearby veins occur here and there, but that does not obscure the apparent regularity of most veins.

Length of veins. The tungsten veins in Kiangsi generally extend both laterally and vertically for long distances. Only a few small deposits are dominated by scattered veins which are several meters to tens of meters long. At most places the common veins or groups of veins are from a hundred to several hundred meters long. In the leading localities some wide veins can be traced for distances up to one thousand meters.

Vertical extent of veins. In Kiangsi, mining operations have not been carried to great depths. Hence direct measurement of the vertical extent of workable ore is almost impossible. But where long and steep-dipping veins extend from the top to the foot of a mountain, and are mined by open pits, drifts, or cross-cuts all along the outcrops, the vertical extent of the workable parts of the veins can be determined indirectly by the difference in elevation between the highest and the lowest workings.

The vertical extent of veins in sedimentary rocks, above granite cupolas or not associated with any igneous exposure, is in general greater than that of veins in granite. In some of the rich tungsten deposits the vertical extent of workable ore in large veins is up to 200 to 350 meters, not considering the possible downward extension into the ground. No downward petering out of the ore content of such veins has been observed, but, at a few places, the topmost portions of such veins become poorer in wolframite and richer in bismuthinite, or more rarely in native bismuth. Of course, this does not necessarily mean that veins in different localities all have a regular bismuth zone above, for the mineral association of these veins varies from place to place.

The extent of the workable ore in some rich deposits that are in smaller granite intrusions has been found to be up to 100 to 200 meters. Where the veins do not extend into the roof-rocks, they are richest immediately below the contact. Within 80 meters or so from the upper contact, the decrease in ore content may be slight. Beyond that, however, the ore becomes perceptibly poorer downward. The low-grade ore in the lower portions may extend for some distance. Thus, the usually low-grade ore found in the superficial parts of great batholiths may be taken as representative of the lower portions of the veins in granite. In case workable ore is found in sediments which occur as roof-pendants on a great batholith, the veins in granite may carry only low-grade ore even immediately below the contact.

In a few localities, molybdenite becomes comparatively more abundant toward the lower extremity of veins, where wolframite gradually peters out.

Strike, dip, parallelism, and intersection of tungsten veins. The tungsten veins of Kiangsi strike generally east-west, and rarely strike outside the sector N70°E to S70°E. Within a single locality, the directions of veins are even more regular.

By sampling eight localities out of 100 deposits, it was found that there was, in addition to the well-developed east-west veins, another system of less important tungsten veins, which strike NNW to N-S, or rarely NNE, and dip steeply. The horizontal angles of intersection between the two systems of veins vary from 50° to 90°. The north-south veins are commonly small, scattered, and discontinuous. But in three localities, the north-south veins are the main productive ones, whereas the east-west veins are either absent or poorly developed.

The two systems of veins were formed, however, during the same period of mineralization, for they do not differ from each other in mineral association or in rock alteration.

All the tungsten veins have steep dips, generally from 70° to vertical. Within each locality, all the veins are either vertical or dip in the same direction and at nearly the same angle. The cross-sections of all the deposits show that the veins are evidently parallel.

As the position of the veins was determined by the attitude of pre-existing fissures, the persistent strike of tungsten veins and the regularity of their lateral and downward extension are due to well-developed, parallel fissures. These fissures are rock joints. They bear a definite relation to the regional tectonics.

The persistent E-W trending, steep-dipping, ore-bearing fissures are developed everywhere in sedimentary rocks. They cut the steep strata at right angles or bisect the various bedding planes at different angles. The direction of the ore-bearing fissures is practically constant throughout the region, though the attitude of bedding planes and the lithology of country rock change considerably from place to place.

Types of Tungsten Deposits

Several types of tungsten deposits are known in southern Kiangsi. The main production is from the pegmatitic-hypothermal veins. Other types, although economically unimportant, may have some scientific interest.

Pegmatite. Pegmatites in southern Kiangsi fall into two distinct groups. One may be ore-bearing; the other is practically barren.

(a) *Common granite pegmatite* occurs in irregular masses in the central as well as in the marginal portions of granite batholiths. Its mineralogical composition is typically simple. It consists essentially of orthoclase or microcline and quartz, with or without a little muscovite. Green or brown micas, tourmaline, fluorite, topaz and ore minerals are practically absent. The rock texture is coarser than that of the adjacent granite, but generally not so coarse as that of the other group of pegmatites, although at places the orthoclase may be as large as a fist. The orthoclase and quartz are tightly interlocked as in ordinary igneous rocks. The orthoclase is mostly hypidimorphic; the quartz is coarsely granular. Drusy cavities do not occur. The wall-rock granite is not greisenized or hydrothermally altered.

(b) *The ore-bearing pegmatite* is so called because it may contain such ore minerals as molybdenite, cassiterite, wolframite, or scheelite. It occurs as irregular dikes, big lumps, pockets or patches, accompanying the main productive veins. The difference in shape between such irregular pegmatites and the regular tungsten veins which occur side by side, is marked. Such pegmatites occur only in small granite intrusions or in the marginal parts of batholiths, and have never been found in the central portion of batholiths where the coarsely porphyritic granite prevails. It consists mainly of orthoclase, quartz, some green or brown mica, and locally some fluorite, tourmaline, and a little ore.

In summary, these ore-bearing pegmatites differ from the common granite pegmatites in occurrence, in texture, in type of wall-rock alteration, and in the presence of pneumatolytic and ore minerals. They are distinguished from the productive pegmatitic-hypothermal ore veins by their dominant orthoclase, comparatively less abundant quartz, insignificant amount of ore mineral, less intense wall-rock alteration, and irregular shape.

Pneumatolytic Replacement Deposits

These deposits are so named because they were formed by the replacement of granitic or aplitic rocks by "pneumatolytic minerals". Locally these deposits contain cassiterite, molybdenite, and occasionally some bismuthinite, wolframite and scheelite. They are described separately.

Cassiterite Replacement Deposits. In many of the tin-tungsten mines of the Yangtaishan zone, a peculiar, mica-rich greisen near the ore veins carries enough cassiterite to justify the mining of the material as tin ore. It is a greenish-gray granular rock of medium texture, and is composed predominantly of lithium-micas or muscovite. It also contains disseminated fluorite, cassiterite, and some molybdenite. In places the rock shows coarse, massive quartz and orthoclase, which being interstitial to the micas, were formed somewhat later than the period of greisenization. Irregular masses of this mica-rich greisen are invariably bordered on one or both sides by the normal greisen, which grades into the unaltered granitic rocks.

This cassiterite-bearing, mica-rich greisen occurs as the wall-rock of tin-tungsten veins, or as irregular patches, lenses, pockets, and rudely tabular bodies associated with the ore veins in the upper portions of granite cupolas.

Veins in the greisen may be only paper-thin, but the greisen itself may be one or two meters wide. At the Sihuashan mine, the greisen locally forms a layer one meter thick at the upper contact of granite with phyllite. There it contains abundant cassiterite and many small quartz stringers, and is connected with the underlying veins. At another place in the same mine, it almost entirely replaces several aplite dikes which were intruded into the phyllite roof-rock above the granite stock. The phyllite wall-rock was left intact. All these irregular masses of mica-rich greisen have been mined for cassiterite.

Veins associated with this greisen are composed of quartz, mica, orthoclase, fluorite, beryl, and topaz, and usually carry as much wolframite as cassiterite. But in the greisen itself, according to the miners, cassiterite is the only ore mineral present. Thin sections of such rocks examined by the writer showed rather abundant cassiterite and fluorite, but little wolframite. Evidently, there was a remarkable difference in the behavior of these two minerals.

Outside the Yangtaishan zone, the tungsten veins do not carry enough cassiterite to justify its recovery. Nor does the mica-rich greisen carry cassiterite and fluorite, although these minerals have been found in a number of other localities outside the Yangtaishan.

Bismuthinite Replacement Deposits. At the Changtienwu mine, north of Shangyou city, wolframite-quartz veins carry a minor amount of bismuthinite, which is recovered as a by-product. In one corner of this mine, an aplitic rock is replaced by greisen, mica-rich greisen, and a network of orthoclase-quartz veinlets. The veinlets themselves do not carry much ore mineral, but the greisens carry abundant bismuthinite which is weathered to bismuthite and bismuth ocher. The ore body is irregular, averaging about ten meters wide. This type of bismuthinite replacement does not occur at other localities.

Wolframite Replacement Deposit. The wolframite replacement deposit was observed only in the Fusseshan Mine, north of Singku city. Wolframite ore is found mainly in pegmatitic-hypothermal veins. Locally, small wolframite crystals and some scheelite grains occur in patches of a greisenized aplitic rock, at the upper contact of granite with phyllite. The surface rock was dug and sluiced for ore. Such an occurrence is similar to the cassiterite-greisen which exists locally at granite-phyllite contacts in the Sihuashan mine. At Sihushan and Shiakeng, 22 miles south of Kanhsien, traces of wolframite are occasionally observed in greisens near the vein contact.

Pegmatitic-hypothermal Veins

The pegmatitic hypothermal veins are almost the only tungsten-producing deposits in southern Kiangsi. They are well-defined, tabular bodies, formed by the filling of pre-existing fissures. They are regular in strike and dip and in lateral and vertical extension. Gangue minerals in these veins include quartz, muscovite and lithium-micas, orthoclase, fluorite, tourmaline, topaz, beryl, albite, sericite, chlorites, and calcite. Primary ore minerals include wolframite, cassiterite, scheelite, pyrite, chalcopyrite, bismuthinite, molybdenite, arsenopyrite, sphalerite, galena, pyrrhotite, native bismuth, magnetite, specularite, tetrahedrite, and stannite. Along the outcrop of veins, or in the upper portions of them, various secondary minerals occur. They include limonite, hematite, kaolinite, pyrolusite, psilomelane, tungstite, bismuthite, bismite, chalcocite, covellite, malachite, azurite, scorodite, marcasite, molybdite, smithsonite, chalcedony, and wood tin.

The texture of the tungsten veins is rather coarse. Tabular crystals of wolframite range from 1 to 5 cm in width, and from a few cm to 30 cm in length, being commonly 3 to 9 cm long. Associated minerals such as lithium-micas, drusy quartz, orthoclase, cassiterite, fluorite, tourmaline, etc., are also coarse. Fine-grained texture is unknown.

Massive quartz makes up most of the veins, in which all other minerals are embedded. Only in drusy cavities does it form coarse crystals. Orthoclase, when present, is commonly in irregular masses, intergrown with massive quartz. As a rule, all the minerals in the veins are unevenly distributed without coating or crustification, but a general sequence of deposition of certain minerals can usually be observed. When veins occur in argillaceous sedimentary rocks, coarse crystals of alkali micas commonly form two distinct bands lining the two walls. Attached to the mica bands are crystals of wolframite, diverging toward the central portion of the vein; then comes the central filling of massive quartz. Iron and copper sulfides, when present, commonly occupy the central parts of the veins or the cracks in massive quartz. Usually in such argillaceous wall-rocks, a thin layer of small tourmaline crystals occurs between the wall and the mica band. Or the tourmaline may form long crystals, extending from the walls toward the center of the vein. In the case of granitic wall-rock, micas in small scales form a very thin layer attached to the walls, and tourmaline is generally absent. In purer arenaceous wall-rocks, mica occurs locally in insignificant quantity.

Drusy cavities occur sparsely in nearly all the veins. Most of them are small and angular. They are commonly bounded by several faces of imperfect crystals of quartz, and have some crystal aggregates of micas in the center. In places, such cavities may be 10 cm across and lined with beautiful crystals of quartz, micas, bismuthinite, fluorite, cassiterite, topaz, scheelite, beryl, arsenopyrite, albite, and orthoclase.

In most places, two stages of mineralization are clearly indicated. Earlier minerals are replaced by later minerals or by groups of later minerals, forming the so-called group replacements. Topaz crystals in the vein are replaced by sericite, sphalerite, galena, and chalcopyrite, most commonly by sericite. Coarse masses of orthoclase are replaced by sericite and chlorite. Commonly orthoclase is intensely replaced by sericite, which forms a light green, waxy, talc-like, crypto-crystalline mass. Greisenized granitic wall-rock may be replaced by patches of chlorite, sericite, and chalcopyrite. At Hungshuichai and Piaotang mines, the group replacement by chlorite, sericite, chalcopyrite, sphalerite, galena, pyrite, tetrahedrite, and stannite is so intense that it obliterates the intergrown structure of earlier minerals, such as feldspars, light-colored micas, topaz and quartz. These earlier minerals are left only as irregular, residual masses surrounded by later minerals. Such group replacements occur at Hungshuichai at the two sides of a large quartz vein which cuts across the tin-tungsten veins and carries quartz and all the later minerals mentioned above. At Shailung mine, northwest of Nankang city, chalcopyrite occurs as large masses in tin-tungsten veins. It attacks coarse crystals of quartz and rounds them. In the Tachishan mine, the tourmalinized wall-rock of tungsten veins is cut here and there by veinlets of chlorite. Sulfides, such as chalcopyrite and pyrite, associated with sericite and chlorite, occur in distinct fractures and veinlets in the tin-tungsten veins in some mines.

Thus, upon the earlier mineralization of the high-temperature tin-tungsten veins in a number of mines, there was imposed a definitely later mineralization, which brought in those minerals that are common in the intermediate vein-zone. Minerals of the earlier stage include quartz, muscovite, lithium-micas, orthoclase, fluorite, tourmaline, topaz, beryl, albite, wolframite, cassiterite, scheelite, pyrite, molybdenite, and native bismuth. The minerals of the later stage include sericite, chlorite, chalcopyrite, pyrite, galena, sphalerite, tetrahedrite, and stannite. Of the later minerals, sericite is the most common. Within each group, there is a sequence of mineral deposition.

The mineral association of the tungsten veins varies in different places. This variation is caused by the following factors:

(1) *Regional variation.* As previously stated, cassiterite and fluorite are common in veins and greisen in many mines in the Yungtaishan zone, but rarely occur outside of this zone. A regional variation in the composition of ore solutions appears to be the only logical explanation of this irregular distribution. Regional variation also explains the dominance of tungsten in Kiangsi and the dominance of tin in Kwangsi, Hunan and Yunnan.

(2) *Chemical composition of wall-rocks.* Light-colored micas and tourmaline are usually abundant in veins with argillaceous wall-rocks. They are insignificant in veins with arenaceous wall-rocks.

(3) *Zoning.* As already stated, a zonal arrangement of bismuth minerals, wolframite, and molybdenite is common in places. In some mines orthoclase-quartz veins may grade upward into pure quartz veins. Pneumatolytic minerals, such as topaz, beryl, fluorite, cassiterite, lithium-micas and muscovite, are more abundant toward the upper portions of veins in granite.

(4) *Later stage of mineralization.* Later mineralization was mainly responsible for the introduction of sericite, chlorites, sphalerite, galena, chalcopyrite, pyrite, tetrahedrite and stannite in the tin-tungsten veins.

Mesothermal deposits and later hydrothermal effects. In the Peshih mine, north of Kanhsien, a large irregular mass of wolframite-quartz ore is found in phyllite. It consists of quartz, small scales of colorless mica, small-bladed crystals of wolframite, some pyrite and chlorite. The quartz is mainly massive, but contains abundant "honey-combed" cavities and small vugs. Colorless mica and pyrite occur in these cavities. Wolframite blades, ranging from 0.5 to 2.2 cm in length, are evenly distributed in the rock. The phyllite wall-rock is locally chloritized. This deposit is no longer mined, for its ore is of low grade. Several hundred meters away from this quartz body are the regular coarse-textured veins, which carry quartz, wolframite, white mica, topaz, and scheelite.

At the Chiulungnao mine, three miles northwest of Hungshuichai, a similar lens-shaped wolframite-quartz body was formerly mined. The ore-body is 50 meters thick in its central position and thins out toward either end. It was introduced along the contact of granite with phyllite. The body is composed entirely of massive quartz with streaks of small, somewhat evenly-distributed wolframite crystals. The phyllite wall-rock is silicified and the granitic wall-rock is greisenized, with dominant quartz and subordinate white mica. Near the quartz body there are many coarse-textured tin-tungsten veins of the high-temperature type, which carry quartz, green mica, wolframite, cassiterite, fluorite, orthoclase, and molybdenite.

At the Hungshuichai mine, a large quartz vein cuts across many tin-tungsten veins and ore-bearing greisens. This vein consists of massive quartz with small amounts of sericite, pyrite, chalcopyrite, sphalerite and galena. Wolframite is reported.

Mineralogy

Wolframite is the only important tungsten mineral in all the mines. The grade of wolframite ore varies greatly in different mines, generally from 0.5 to 3.5 per cent WO_3. The ratio of FeO to MnO in the wolframite varies in different localities. Analyses of the 93 per cent pure concentrates indicate that this ratio approaches 2:1 at the Kweimeishan mine, 3:2 at Pankushan and Sialung, 1:1 at Tachishan, and 2:5 at Shangping.

In general, wolframite crystallized later than tourmaline and zinnwaldite. The latter two minerals often line the walls; and, attached to them, grow the wolframite crystals. Both mica and tourmaline crystals are frequently penetrated by wolframite blades. The latter are generally earlier than quartz, orthoclase, scheelite, and all sulfides except molybdenite. Its crystals are embedded in massive quartz, and are occasionally in massive orthoclase. Replacement of wolframite by scheelite is common. The former is also commonly penetrated or replaced by pyrite, pyrrhotite, arsenopyrite, bismuthinite, chalcopyrite, and other sulfides. The crystallization periods of wolframite and cassiterite overlap. At places, cassiterite lines the walls, wolframite filling the central spaces; at other places, the reverse is true. At Hungshuichai, wolframite crystals are replaced by massive cassiterite along their cleavages and fractures.

Scheelite is present in most wolframite-quartz veins, but only in insignificant quantities. It constitutes from a fraction of a per cent to about three or four per cent of the wolframite concentrates from various localities. It often replaces wolframite along its crystal boundary and cleavage. Intense replacement leaves wolframite as residual masses inside scheelite. The latter is commonly penetrated or replaced by pyrite, pyrrhotite, and chalcopyrite. At some localities it occurs as minute crystals lining cavities inside wolframite crystals, or deposited in vugs upon chlorite. Most of the scheelite is believed to be primary.

Quartz is the main constituent of all tungsten veins. It constitutes from 90 to 97 per cent of the total volume of the ordinary veins. The crystallization period of the massive quartz is later than that of tourmaline, zinnwaldite, topaz, beryl, orthoclase, molybdenite, wolframite, cassiterite, bismuthinite, and native bismuth, and overlaps the crystallization periods of fluorite, arsenopyrite, pyrrhotite, magnetite, and some pyrite. But it is definitely earlier than that of chalcopyrite, pyrite, sphalerite, galena, tetrahedrite, stannite, sericite, chlorite, and calcite.

In the mica-rich greisens, quartz is generally absent, though in some sections of such rocks several grains of residual quartz are visible. Near the vein contact, such greisens may contain some interstitial quartz and orthoclase in addition to the mica, fluorite, and cassiterite. This clearly indicates that quartz and orthoclase formed after the period of greisenization. Thus, the advanced pneumatolytic metamorphism and replacement is a phase slightly earlier than, and different in nature from, the introduction of the ultra-siliceous solution which formed the common wolframite-quartz veins.

Cassiterite is a common constituent of the tungsten veins in the Yuntaishan zone. At many localities in this zone, it is rich enough to justify its recovery. Some veins carry even more cassiterite than wolframite. Cassiterite occurs in veins as well as in mica-rich greisens. It is invariably associated with fluorite. The amount of cassiterite varies proportionately to that of fluorite. There is no exception to this rule. Unlike cassiterite, wolframite bears no apparent relation to fluorite. In several rich tin-tungsten deposits cassiterite appears in irregular masses intergrown with and replacing wolframite. In many tin-tungsten lodes, cassiterite is richer in the upper horizons but peters out downward more rapidly than wolframite in the same lodes.

Tungstite is a secondary mineral after scheelite or, less commonly, after wolframite. Scheelite in many places is partly altered to a light yellow or greenish yellow, powdery tungstite.

Limonite, psilomelane, and pyrolusite are secondary minerals, frequently found in the upper parts of tungsten veins.

Bismuth ocher and molybdite. Bismuth ocher is a common weathering product of bismuthinite and native bismuth. Molybdite is a weathering product of molybdenite.

Chalcedony forms botryoidal masses lining cavities along the outcrops of certain tungsten veins.

Orthoclase is the main constituent of the ordinary granite pegmatites and the ore-bearing pegmatites. In the pegmatitic-hypothermal tungsten veins, orthoclase either occurs in small quantities or is entirely absent. Only in rare cases does it amount to more than one-fifth of the total volume of the veins. In general, veins carrying notable amounts of orthoclase are near the granite exposures, but the reverse statement is not true. In places, wolframite-quartz veins with notable amounts of orthoclase change upward into veins without orthoclase. Crystals of muscovite, zinnwaldite, wolframite, topaz, tourmaline, cassiterite, and molybdenite are sometimes surrounded by massive orthoclase. At the Shangping mine, many veins contain abundant orthoclase and zinnwaldite, together with quartz and wolframite.

Albite occurs generally as minute inclusions in orthoclase. Occasionally it occurs as small anhedrons intergrown with orthoclase, or as small tabular crystals in the vugs of veins.

Zinnwaldite, muscovite, and lepidolite. The light-colored micas, with the exception of sericite, are especially important in the tungsten deposits of southern Kiangsi. They are invariably present in the ordinary pegmatitic-hypothermal tungsten veins, in the altered wall-rocks, and in the ore-bearing pegmatites. They constitute less than 1 per cent to nearly 20 per cent of the total volume of the tungsten veins, ordinarily about 1 per cent or less. They constitute over 90 per cent of the mica-rich greisens, 20 to

45 per cent of the normal greisens, and less than 1 per cent to 60 per cent of the altered sedimentary wall-rocks. They occur in varying amounts in ore-bearing pegmatites.

Zinnwaldite, or muscovite, is one of the earliest minerals in sequence of deposition. It is later than spinel, biotite, and andalusite, which formed through the recrystallization of materials in the wall-rock, and somewhat later than tourmaline, which may occur as inclusions in mica, but is earlier than all the other vein-forming minerals.

Biotite has never been found in veins or pegmatites in southern Kiangsi. The occurrence of biotite near tungsten veins is limited to the recrystallized wall-rocks, which were argillaceous sediments, diorite, monzonite, or occasionally granite. In argillaceous wall-rocks, biotite occurs as minute grains associated with fragmental quartz. The whole mass is then replaced by metacrysts of muscovite and tourmaline.

Topaz is associated with quartz, zinnwaldite, fluorite, beryl, and orthoclase. Aggregates of topaz are sometimes molded around quartz crystals. In places, it occurs as inclusions in massive orthoclase, or is surrounded by fluorite. Narrow veins with zinnwaldite lining the walls and a central filling of topaz aggregates are observed at the Piaotang tin-tungsten mine. Being one of the earliest minerals, topaz is often replaced by sericite, chlorite, sphalerite, chalcopyrite, pyrite, and galena along its cleavage planes, cracks, and grain boundaries, forming the so-called group replacement. The replacement of topaz by sericite is most characteristic, being frequently observed under a microscope.

Beryl is present in small quantities in many tin-tungsten mines of the Yuntaishan zone. It occurs in veins which are introduced either into granite or into sediments. It forms long, prismatic, hexagonal crystals, embedded in massive quartz or in druses. Largest perfect crystals are up to 7 cm in length and 1 cm in diameter. More commonly, it appears as coarse, irregular masses which are intergrown in massive quartz and also associated with topaz, muscovite, fluorite, wolframite, cassiterite, and orthoclase. Crystals of wolframite, muscovite, cassiterite, molybdenite, and topaz are found embedded in massive beryl. Beryl is quite abundant in cassiterite-wolframite veins in the southern part of Sihuashan.

Fluorite. In tin-tungsten deposits, fluorite is invariably present in the veins, greisens, and the altered granite or sedimentary wall-rock. In deposits which are rich in cassiterite, fluorite occurs in abundance, whereas in those without noticeable cassiterite, fluorite is rarely present, either in the veins or in the wall-rock. It also forms coarse masses, closely associated with cassiterite, wolframite, molybdenite, micas, and orthoclase embedded in massive quartz. In such occurrences, fluorite appears to be later than all the other minerals mentioned. In the mica-rich greisens, fluorite and cassiterite are closely associated; but the former spreads out into the granite wall-rock much farther than the latter. The former, associated with white mica, replaces the feldspars and biotite in the zone of altered granite, whereas the latter occurs only in the intensely greisenized wall-rock.

Bismuthinite. Most of the tungsten veins in southern Kiangsi contain a little bismuthinite, but only in eight localities is it recovered as a byproduct. In 1937, these deposits yielded about 70 metric tons of bismuth concentrates averaging 60 per cent bismuth. The production can be increased when methods of concentration are improved. Veins carrying recoverable bismuthinite are the same type of wolframite-quartz veins as found elsewhere in southern Kiangsi. They were introduced into sedimentary rocks as well as into granite. But usually such veins contain no recoverable cassiterite and very little molybdenite and feldspar. Tourmaline, topaz, and fluorite are sometimes observed in such veins, but rarely in large quantities. A little pyrite is generally associated with bismuthinite. In several localities, bismuthinite is impregnated into the greisenized granite or aplite wall-rock. At Nanling mine, greisen with abundant disseminated bismuthinite is mined and sluiced for bismuth ore. As a rule, bismuthinite and wolframite in veins show vertical zonal distribution, the former being richer in the upper horizons and the latter in the lower.

Molybdenite is present in many tungsten mines. It is comparatively abundant at Sihuashan, Hungshuichai, and neighboring localities, and at Yangsikeng, some twenty miles southeast of Kanhsien. Even in these places, it constitutes only a small fraction of 1 per cent of the vein material. It occurs in pegmatites, mica-rich greisens, pegmatitic-hypothermal veins, and in the greisenized granite or aplite wall-rock. In wolframite veins, it is more abundant in the lower horizons where wolframite gradually disappears. Veins carrying the most molybdenite occur chiefly in granite. Such veins usually contain some orthoclase, but very little bismuth minerals.

Pyrite is present in most tungsten mines, constituting only a small fraction of a per cent in wolframite ores. It occurs as aggregated crystals or granular masses, embedded in massive quartz or filling the fractures of veins. Not uncommonly, it fills the inter-crystal spaces of wolframite, or forms veinlets or patches cutting or replacing the latter. Where closely intergrown with chalcopyrite, pyrrhotite, arsenopyrite, or sphalerite, it develops euhedral forms surrounded and corroded by the other sulfides.

Arsenopyrite is much less common than pyrite. It is most abundant in wolframite veins at Sihuashan, Siaolung, Shialung, and Hungsuichai. Even in these localities, however, it constitutes no more than 1 per cent in the crude ores. Analyses of the ore concentrates show that arsenic ranges from 0.020 to 0.422 per cent. Only at the Yaokangsien mine in eastern

Hunan province do the upper parts of wolframite veins carry abundant arsenopyrite, from which arsenic is recovered as a by-product. In such localities, arsenopyrite is removed from wolframite ores by hand-picking before finer crushing. Where intergrown with galena, chalcopyrite, or sphalerite, it is penetrated and replaced by them. In the oxidized zone, at Sihuashan, arsenopyrite is partly replaced by secondary scorodite and native sulfur.

Pyrrhotite was found in tungsten veins at Tachishan, Shialung, and Siaolung. It occurs as masses surrounding wolframite, pyrite, and arsenopyrite, and traversed by chalcopyrite veinlets.

Chalcopyrite has been found in many localities; but in only three tin-tungsten mines, namely Shialung, Piaotang, and Hungshuichai, is it comparatively abundant. Several veins at Shialung, some 30 miles ENE of Tayu, carry about 4 per cent copper in the form of massive chalcopyrite. This mineral is usually intimately associated with chlorite, sericite, pyrite, sphalerite, galena, and occasionally tetrahedrite and stannite. These minerals were introduced during a mesothermal stage which was definitely later than the pegmatitic-hypothermal phase represented by the formation of wolframite, cassiterite, molybdenite, bismuthinite, quartz, feldspars, muscovite, lithium-micas, tourmaline, topaz, beryl, and fluorite. Many of the earlier minerals are universally present in ore veins, whereas the later minerals appear only in certain localities and in certain parts of some veins, filling fractures in these veins and replacing the earlier minerals.

Chalcopyrite appears as irregular masses, filling the fractures of veins, and as veinlets and networks which replace the various vein-forming minerals. It replaces quartz, feldspar, topaz, fluorite, beryl, scheelite, bismuthinite, and molybdenite. Cassiterite and wolframite are sometimes engulfed and partly replaced by chalcopyrite. Coarse drusy crystals of quartz are not infrequently enclosed and rounded by massive chalcopyrite. Greisens in several places are locally replaced by chalcopyrite which is in close association with chlorite, sericite, and later sulfides. Pyrite and arsenopyrite crystals, surrounded by chalcopyrite, are sometimes strongly corroded by the latter. It may traverse pyrite, pyrrhotite, arsenopyrite, or sphalerite in veinlets. Sphalerite from various localities almost invariably contains minute inclusions of chalcopyrite. Supergene alteration of chalcopyrite gives rise to covellite, chalcocite, limonite, malachite, and azurite.

Sphalerite occurs quite abundantly at three tin-tungsten mines, namely Piaotang, Hungshuichai, and Shialung. Traces of it are found in several other localities.

Galena is closely associated with sphalerite.

Marcasite is a secondary mineral found at the Tachishan and Shialung mines.

Chalcocite and covellite are secondary minerals after chalcopyrite.

Native bismuth occurs in tungsten veins at Talungshan, five miles southwest of Piaotang; Naling, three miles south of Changtienwu and Changtungkeng, three miles south of Hungshuichai. In these mines, bismuth, amounting to from 0.07 to 0.5 per cent of the vein material, is picked out as a by-product by hand. Like bismuthinite, native bismuth is comparatively more abundant in the upper horizon of wolframite veins and gradually fades out downward.

Bismutite is a common secondary mineral in tungsten veins, being derived through the oxidation of bismuthinite or native bismuth. It is present in small quantities in nearly all tungsten mines.

Malachite and azurite are secondary minerals formed by the oxidation of chalcopyrite in the upper portions of veins.

Scorodite has been found only at Sihuashan.

Brief Description of Some Deposits

Tachishan wolframite ore occurs in veins which were formed by the filling of two sets of rock joints, one of which strikes N 65°–80° W and dips 65°–80° northward, and the other of which strikes N 10° E to N 25° E, and dips steeply westward.

The veins consist mainly of quartz, with some wolframite and zinnwaldite. Some pyrite, scheelite, chalcopyrite, and a little tourmaline, white feldspar, cassiterite, molybdenite, bismuthinite, and sphalerite are accessories. Sericite and chlorite occur locally. The wall-rock is heavily tourmalinized. The veins occur in sheeted zones. The most productive part is near Aotzuchieh, where some 24 parallel veins, with an aggregate thickness of 9.6 meters, occur in a zone 90 meters wide. The individual veins are from 0.15 to 1.5 meters thick, and some large veins have been traced continuously for 650 meters along the strike. At Shushanwe, twenty parallel veins, each 0.10 to 1.0 meter thick, with an aggregate thickness of 5.6 meters, occur in a zone 270 meters wide. Many small scattered veins are found in other parts of the district. All the quartz veins carry ore, but the ore mineral, wolframite, is unevenly distributed in the veins. Neither petering out of the ore nor thinning out of the veins has been found, even in the deepest workings in the district. The ore averages about 2.5 per cent wolframite.

Kweimeishan. The veins strike N 20° W and dip steeply eastward. They occur in a sheeted zone 1,500 meters long and from 200 to 500 meters wide. Veins are thicker in the middle part of the zone and become gradually thinner toward both ends. The most productive part is near Ma-ao, where some 30 parallel veins with an aggregate thickness of 20 meters occur within a zone 200 meters wide. The veins are composed mainly of massive quartz with wolframite, and are characterized by the striking scarcity of other associated minerals. Traces of muscovite, pyrite, chalcopyrite, bismuthinite and cassiterite, however, are found in places. The wall-rock is slightly tourmalinized. The ore averages about 2.9 per cent wolframite; some parts carry even 10 per cent. The veins are worked from the top of the mountain by many shafts, some of which have reached a vertical depth of 90 meters, and no decrease in the grade of ore nor any thinning out of the veins has been found. The vertical extent of workable ore seems to be considerable, probably more than 200 meters from the outcrops.

Sihuashan. The deposit is located on the southern part of a granite stock, which covers an area about 6 kilometers in diameter. There are three other similar tungsten deposits which are located respectively on the eastern, northern and northwestern borders of the same granite stock. Nearly all the tungsten veins occur in granite, and end abruptly at the granite-phyllite contact. No distinct contact metamorphism of the phyllite or of the granite is observed. South of Hsia-ao at Sihuashan, some aplite dikes, which intruded the phyllite and were later greisenized, carry cassiterite and fluorite. Tabular greisen bodies formed by replacement of granite and consisting mainly of muscovite, fluorite, and cassiterite, occur in granite at several places at Sihuashan.

The mining area at Sihuashan is about 2,000 meters long from north to south and 1,200 meters wide from east to west. Within this area, ore veins are numerous, all striking N 70° E to E and dipping 70°–90° northward. Searches along several N–S lines from south of Hsia-ao to north of Toun-tung disclosed some 200 parallel veins, excluding those less than 10 cm thick. They are from 10 cm to 2 meters thick, mostly from 15 to 40 cm thick, and have an aggregate thickness of 51 meters. Some wide veins have been traced for 1000 meters along their strikes, whereas narrow veins are much shorter and are discontinuous. All of them carry wolframite and are, or were, mined along their outcrops by numerous small open pits.

The veins consist mainly of quartz, with some orthoclase, wolframite, muscovite, and a little cassiterite, molybdenite, arsenopyrite, pyrite, scheelite, chalcopyrite, galena, bismuthinite, beryl, topaz, fluorite, sericite, and chlorite. There are notable changes in mineral composition and rock alteration at different horizons of the veins. Generally speaking, at the topmost parts of veins, greisenization of the granite wall-rock is most intense; wolframite, cassiterite, fluorite, topaz, and beryl are most abundant, whereas orthoclase and molybdenite are scarce or absent. Toward the deeper portions of the veins, the granite wall-rock is only slightly altered, the normal greisen being narrow or absent; orthoclase and molybdenite are more abundant; cassiterite, fluorite, topaz, and beryl are scarce, and the amount of wolframite falls off. In this district, the richest ore is along the contact of the granite with sediments. Veins on the southern and southwestern border of the granite body, and those on the ridges with small roof-pendants of phyllite, carry good ore, whereas veins exposed on the bottom of gulches and those on the northern and northwestern border of the area, which are farther from the contact, carry ore of much lower grade. Obviously, no great depth of commercial ore can be expected in this district. However, it is not a suitable locality for deeper mining, although it has been yielding a good tonnage of ore, with numerous veins over a large area.

Hungshuichai. This deposit and several other tin-tungsten deposits are located on the southern border of a granite stock, which intruded pre-Devonian argillaceous and arenaceous sediments which are now complexly folded and metamorphosed. The mineralized zone at Hungshuichai is a narrow shear zone in coarse-grained biotite granite. It is 650 meters long and from 20 to 80 meters wide, trending N 40° W. Mineralization in the granite does not extend to the roof-rock of mica schist. The outcrop of the mineralized zone has a slope of 20° toward the southeast, following the granite-schist contact.

Within the mineralized zone, no fresh granite can be observed; the rock was changed completely into a normal greisen of greenish gray color, with many pockets, patches, and dikelets of dark-gray, mica-rich greisen and numerous ore veins. The normal greisen in places shows distinct gneissic structure, due to the parallel arrangement of the elongated, lens-shaped quartz and the light-colored mica. This foliation strikes N 10°–20° E and dips 70°–80° ESE. The greisen shows a cleavage parallel to the foliation, and a set of well-developed gash joints. The gash joints, but not the cleavages, were followed by ore veins which strike N 70°–80° W and dip 60°–90° northward. All the ore veins trend in the same WNW direction, even where the greisen does not show any distinct gneissic structure. The coarse-grained biotite granite surrounding the mineralized zone does not show any noticeable parallel arrangement of minerals.

The ore veins are arranged *en echelon* and transect the narrow greisenized shear zone at angles of 30 to 40°, with extension direction of the latter. Within this zone the veins are closely spaced. They are from several cm to 3 meters thick, irregular and lenticular in form, and thin out toward the borders of the greisen zone. The aggregate thickness of ore veins in the zone varies from 5 to 12 meters. Wolframite is produced mainly from the veins, while cassiterite is produced from both the veins and the mica-rich greisen. The normal greisen also contains a little cassiterite, which is not saved in mining. The veins consist mainly of quartz, orthoclase, greenish mica, fluorite, cassiterite, and wolframite, with some beryl, topaz, sericite, chlorite, molybdenite, pyrite, chalcopyrite, arsenopyrite, sphalerite, galena, scheelite, and bismuthinite. The mica-rich greisen consists mainly of light-green and golden-yellow mica, fluorite, and cassiterite, with some orthoclase, topaz, molybdenite, and a little wolframite. The normal greisen is composed mainly of quartz and mica, with a little fluorite, cassiterite, and red garnet. South of Chungao, a wide quartz vein, of later hydrothermal stage, consisting mainly of quartz, sericite, chlorite, and sulfides, cuts across the numerous high-temperature tin-tungsten veins. Near this quartz vein, sericite, chlorite, and sulfides are abundant and replace the earlier minerals.

Piaotang. The country rocks here are pre-Devonian dark-gray quartzite and purplish-gray phyllite, which are closely folded and complexly faulted, with a prevailing strike of east-northeast and steep dips. A quartz monozonite boss and a diorite dike are exposed near the mining district. The quartz-monzonite grades into quartz diorite on its border. No granite exposures are found within several kilometers of the district. Tin-tungsten veins occur in phyllite and sandstone, following transverse joints and faults. The purplish-gray argillaceous rocks adjacent to the closely-spaced veins are altered to a dark greenish-gray, medium-grained hornfels composed mainly of zinnwaldite, with some fluorite, quartz and tourmaline. All the veins strike east-west and are vertical. The most productive part is a narrow sheeted zone, extending from Shanniulung to west of Aipesheh. This zone is about 700 meters long from E to W, and from 20 to 40 meters wide. Within this zone are found some 30 to 50 closely-spaced ore veins, from several cm to 70 cm wide, and aggregating 2 to 5 meters in width. This zone is mined by open pits and glory holes. Some scattered veins occur north of this zone and are also mined. The veins are composed of quartz, zinnwaldite, fluorite, cassiterite, wolframite, topaz, chlorite, sericite, sphalerite, chalcopyrite, pyrite, galena, orthoclase, calcite, arsenopyrite, bismuthinite, scheelite, and a little tetrahedrite and stannite. The cassiterite-wolframite ore is of high grade and the vertical extent of the ore appears to be considerable.

Shangping. The sedimentary rocks here are purple phyllite intercalated with thin-bedded sericitic sandstone and gray quartzite of Siluro-Ordovician age. They strike north by west and dip steeply westward. A small boss and a dike of intensely sericitized granite porphyry occur on the north side of the district. Tungsten veins occurring in phyllite and sandstone on the top of a mountain strike east-northeast to east-west and dip steeply. They were formed by filling the transverse joints or tension cracks of the steep-dipping sediments. The veins consist mainly of quartz, orthoclase, and zinnwaldite, with some wolframite. Traces of topaz, fluorite, cassiterite, sericite, pyrite, and chalcopyrite are found in places. The veins are characterized by abundant orthoclase and scarcity of sulfides. Orthoclase amounts to about one-third of the volume of veins, and some parts of the veins are composed entirely of massive orthoclase with some zinnwaldite and wolframite. The wall-rock is intensely tourmalinized and contains secondary zinnwaldite.

Ore veins occur in a sheeted zone 900 meters long from east to west and 150 meters wide. Within this zone, some 50 parallel but discontinuous veins occur, excluding those which are less than 10 cm thick. They are from 10 to 70 cm wide, and have an aggregate thickness of about 13 meters. These veins are mined by many cross-cuts and drifts. Adits are driven from each side of the mountain and at different levels within a vertical distance of 80 meters from the mountain top. The veins within 50 meters from the top of the mountain have been nearly exhausted. The grade of ore is from 1.5 to 2 per cent wolframite. Since there is no decrease in the tenor of ore in deeper workings, and since some veins on the western end of the sheeted zone are being worked at a level 180 meters lower than the top of the mountain, it seems probable that the mining here can be carried downward for another 50 to 100 meters.

Pankushan. In the vicinity, no igneous exposures have been found. The nearest granite exposure so far found is the granite stock of Tieshanlung, about 20 kilometers to the northeast. Ore veins occur in a brownish-yellow, thick-bedded sandstone intercalated with a little sandy shale. The Devonian sandstone, lower Carboniferous shale, and Permo-Carboniferous limestone in the vicinity form an elongated, semi-circular structural basin which is bounded on the south by a large transverse fault. The mining district is on the southeastern border of the structural basin and is about a kilometer north of the transverse fault. Beds in the mining area strike NW and dip 15° to 60° southwest, the dip being gentle on the top of the mountain and steeper on the southern slope. The veins strike N 70°-80° W and dip 80° southward, cutting the sandstone beds obliquely.

The veins consist mainly of massive quartz, with wolframite, bismuthinite, a little zinnwaldite, pyrite, chlorite and scheelite, and traces of sericite, chalcopyrite, and sphalerite. The veins are characterized by scarcity of mica and by considerable bismuthinite, which has been weathered to bismutite in the upper portions of veins. Wolframite occurs in large columnar crystals, locally filling the entire vein. Concentrates are mainly cubic fragments of nearly pure wolframite, up to an inch across. The sandstone wall-rock adjacent to the veins is slightly altered, but some interbedded argillaceous rocks carry tourmaline and some secondary zinnwaldite.

The main productive area is on the southern slope of Pankushan, where a sheeted zone, 1,100 meters long from east to west and 250 meters wide, contains 21 closely-spaced veins which are from 0.2 to 3.5 meters wide, and have an average aggregate width of 11 meters. Some wide veins have been traced for 1,100 meters along the strike, but narrow veins are shorter. The veins are mined mainly by shafts. The deeper shafts have reached a vertical depth of 80 meters, but the average depth reached by most shafts is about 40 meters. The grade of the tungsten ore is said to increase with depth. The ore averages more than 2.5 per cent wolframite. Some parts of the veins consist almost entirely of wolframite. The vertical extent of workable ore seems to be great. Judging from the fact that the lowest height of the vein outcrops in the same sheeted zone are being profitably mined, it is suggested that the mining can probably be carried downward for another 200 meters.

Bismuth ore, consisting of bismuthinite and its weathering product, bismutite, is a by-product of the tungsten mines on the southern slope of Pankushan. In these mines, bismuth ore, containing 60 per cent bismuth, as recovered by a rough hand-picking, amounts to about 0.1 per cent of the ore mined. On the top of Pankushan, locally called Lungwangshan, which is some 270 meters higher than the average height of vein outcrops on the southern slope, there are four narrow veins, formerly mined by open cuts, primarily for bismuth. The veins have an aggregate width of 0.6 meter and are 250 meters long. They are said to carry some 1.5 per cent bismuth carbonate and less than 1 per cent wolframite.

The following table gives the approximate yearly pre-war productions of the five principal mines in Kiangsi Province. (Huamaiau, not shown in map on p. 25, is located in the granite region north of Yinkeng).

Mine	Approximate Production in Tons (65% WO_3)	Approximate Grade of Ore (% WO_3)	Principal Associated Mineral
Sihuashan	15,000	0.8	Molybdenite
Tachishan	1,000	2.0	
Kueiweishan	500	1.0	
Paukushan	500	1.5	Bismuthinite
Huamaiau	800	1.5	Pyrite

Hunan Province

Topographically and geologically the southeastern part of Hunan, in which most of the important deposits of this province are found, is a part of the Nanling region.

The Tzehsing deposit (Yao-kang district) is the most important one in Hunan. It is to be noted that this is the place where tungsten was first discovered in China. The geology of this region is characterized by two prominent series of sedimentary rocks: Devonian quartzose sandstone and

Carboniferous limestone and coal series, which were intruded by a huge mass of granite. Associated with the wolframite mineral are arsenopyrite, iron pyrite, chalcopyrite, malachite, galenite, zincblende and a small amount of bismuthinite.

The quartz veins which carry wolframite are of two types, those occurring in the granite itself and those occurring in the quartzose sandstone near the contact with the granite mass. The veins generally strike NW-SE and dip 60°. The thickness of the workable veins ranges from 0.2 to 2 meters.

Deposits of less importance are found in Lei-tze-ling (Liu-wu district), Wu-King-Ping (Shangning) and King-chuan-tang (Chen-hsien). The ore-bearing quartzose veins found in these districts occur only in the granite batholith and their thicknesses vary from 0.1 to 0.3 meter.

Kwangtung Province

The occurrences of tungsten deposits in Kwangtung may be conveniently grouped into the following five regions:

(1) Northern Region: deposits are found in the districts of Weng Yuan, Yo Chang, Kok Kang, Yin Fa, Chih Hsing, Yu Yuan, Lin Shon, Ying Tak, Nam Hung.

(2) Western Region: deposits are found in the districts of Yuan Fu, En Ping, Lo Ting, Fung Chuan, Sin Hsing.

(3) Central Region: deposits are found in the districts of Tsung Hua, Chin Shing.

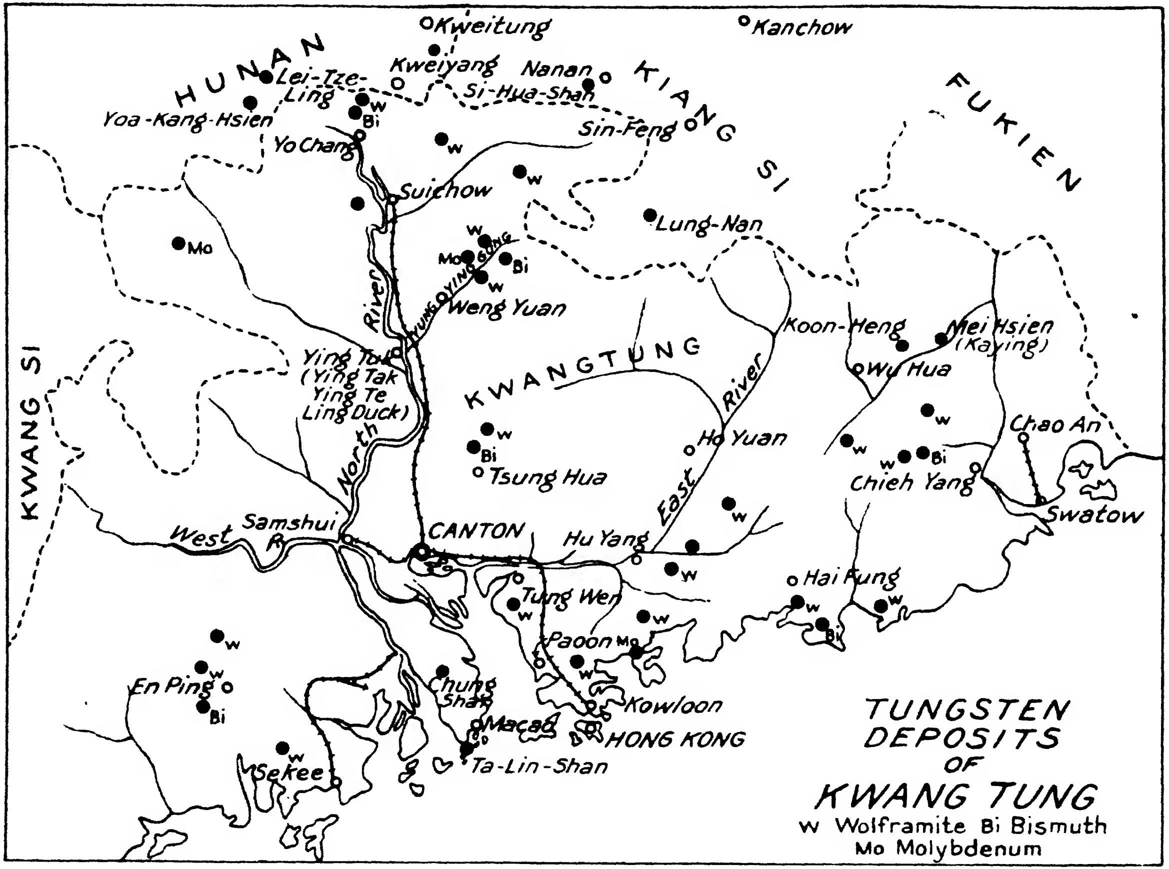
(4) Eastern Region: deposits are found in the districts of Mei Hsien, Fung Shun, Hsing Ning, Wu Hua, Chih Chin, Ho Yuan, Lin Ping, Wo Ping.

(5) Coastal Region: deposits are found in the districts of Chao Yang, Chao An, Chieh Yang, Tai Shan, Hai Fung, Wei Yang, Pao An, Tung Wen, Sin Hue, Lu Pa, Chung Shan, Kowloon.

A few common characteristics of the important Kwantung deposits are here described.

Weng Yuan District. The Weng Yuan tungsten and bismuth mines are located 70 li (25 miles) northwest of the city of that name. An igneous rock, mostly granite, is intruded between Devonian sandstone and shale, and is exposed over an area of 60 li long and 40 li wide. The quartz vein, carrying bismuth and tungsten, cuts the granite and extends over a distance of about 20 li. There are four parallel branches of this vein, which are respectively 200, 400 and 500 feet apart. The first branch has been extensively mined and is from eight inches to one foot wide. The proportion of tungsten to bismuth mined is roughly 8 to 1.

Yo Chang District. The tungsten and bismuth mines are located at



Tungsten deposits of Kwang Tung.

Feng-men-wa, 25 li north of Yo Chang City. Granite is intruded into the Permian sandstone and shale. In the granite four parallel quartz veins have been found which are 20, 30 and 32 feet apart, respectively. The longest has an extension of about 3½ li. The veins strike N 63° W and dip 82° southwesterly. The first and second veins are a foot, the third is four inches and the fourth nine inches wide.

En Ping District. At Po Chi Shan there are found in the granite two parallel quartz veins, which are about 10 feet apart striking E-W and dipping 70° S. They have a thickness of about 6 to 7 inches.

Pao An District. At Ju Heng, two quartz veins 3 feet apart and 4 inches and 6 inches thick, respectively, are found cutting a purple-reddish sandy shale, probably of the Triassic age. Besides the wolframite, a small quantity of native bismuth is mined from the veins.

Kwangsi Province

Most of the wolfram deposits occur in the eastern part of Kwangsi Province, in the districts of Bing Yang, Kung Shing, Sin To, Teng Hsien, Hwai Chi, Fu Chuen and Ho Hsien. The geology of the deposits in Kwangsi is similar to that of the Kwangtung deposits. In Fu Chuen and Ho Hsien, besides the vein deposits there are very rich placer deposits. The ores mined in these two districts contain tin and wolfram in the proportion of 20 to 1 respectively. Up to the present, the Sin To deposits are considered to be the richest in this province. In this district there are more than 60 parallel veins, averaging 0.20 meter in width, 35 meters in length and 60 in depth.

Yunnan Province

Yunnan's tungsten production has a comparatively short history, for the first prospecting was done in 1935. The most important deposits are located at Ching Hsu and Shek Ping, about 180 kilometers south of Kunming, near Montze. The ore is a mixture of scheelite, wolframite and some ferberite, with scheelite predominating.

BURMA

As a tungsten-producing country Burma once ranked next to China.* Her output in wolfram from 1913 to 1937 amounts to 17.4 per cent of the world production, of which the Mawchi Mine alone contriubtes roughly 60 per cent.

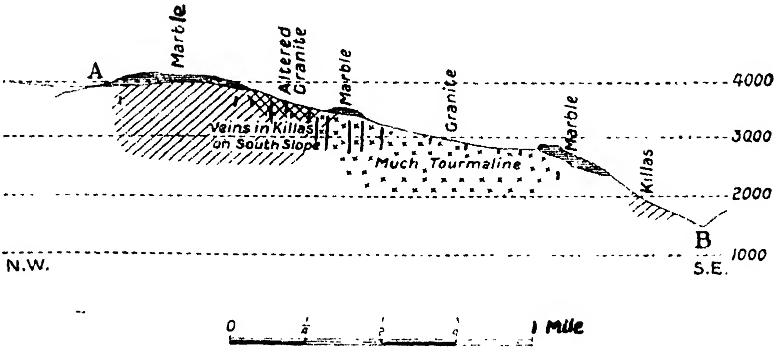
Lower Burma, the Malay Peninsula and Thailand belong in a general way to a single geological structural unit. During late Jurassic or Cretaceous time, the palaeozoic and older rocks were invaded by granite intrusion, which gave rise to deposits of tin and tungsten.

---

* The United States is now second to China.

Mawchi

The Mawchi tungsten deposit is located in the Keren Hills in the native state of Karenni. In this area are found the killas (argillites and fine sandstones), limestone and dolomite, with intrusions of granite. The following figure shows the geology of this area.



Section A-B along Granite Ridge, Mawchi.

The number of lodes so far known is about 60. They consist of a series of vertical parallel quartz veins in tourmaline-granite and killas, striking NNE over a length of several hundred feet, and are from $3\frac{1}{2}$ to 5 feet in width, averaging less than 4 feet. With one exception, the veins rapidly die out on meeting the overlying limestone.

The valuable minerals contained in the ore are cassiterite, wolfram and scheelite. The other, non-valuable minerals are pyrite, arsenopyrite, chalcopyrite and galena, all in small quantities. In still lesser quantities are found molybdenite, sphalerite, bismuthinite, covellite, chalcocite, cerussite and tungstite. The main gangue mineral is quartz; associated with it are calcite, tourmaline, muscovite, chlorite, fluorite, beryl, garnet, zoisite, orthoclase and kaolinite.

The run of mine ore generally has an assay value of about 2.5 per cent mixed tin and tungstic oxide, in approximately equal proportion. Scheelite shows two modes of occurrence: in one it replaces wolfram and in the other it occurs interstitially in the latter.

With regard to the process of mineralization at Mawchi, reference has to be made to the very illuminating article on "Tin-Tungsten Mineralization at Mawchi, Karenni States, Burma", by Dr. J. A. Dunn. To quote:[20]

"Mineralization at Mawchi has taken place in two ways—impregnation of cassiterite throughout the granite, and formation of the mineral veins. Both forms of mineralization did not necessarily take place at the same time.

"It is a curious fact that although disseminated SnO_2 is so wide-spread throughout these granitic rocks, wolfram has not been similarly detected. Wolfram does, however, occur in certain segregations which are commonly found in the granite. These segregations consist of cassiterite, wolfram (usually considerably replaced by scheelite), tourmaline and completely kaolinized feldspars—one such segregation contained 22.6 per cent Sn and 6.23 per cent WO_3. Other segregations consist of tourmaline and quartz with a little cassiterite. These segregations may be regarded as of the nature of local pockets of final magmatic liquid, and in which sometimes WO_3 was concentrated along with the other constituents; its replacement by scheelite in these segregations is comparable with the relation between these minerals in the lodes and is presumably a matter of stability at lower temperature.

"In view of the abundance of wolfram in the lodes, its apparent absence in the granite compared with cassiterite requires explanation. It is assumed that the Sn-bearing molecule in the magma would be much more volatile than the WO_3 molecule; in other words its vapour pressure is higher. Towards the end of crystallization of the magma the greater part of the remaining liquid would be concentrated in the lower part of the magma reservoir but, with any tendency to pressure relief, the more volatile constituents would rise through the crystallizing granite, in which there is sufficient liquid-filled pore-space to permit the ready movement of gases. Thus, the final liquid in the pore-spaces of the crystallized granite may acquire a certain proportion of Sn, whilst the less volatile WO_3 is relatively absent from them, although concentrated in the deep-seated residual liquid.

"It is not supposed that these deuteric changes took place in the granite only after most of it had crystallized. As the magma crystallized downwards and inwards from its roof and sides, these changes would be taking place in the crystallized rock. It is possible that some of the cassiterite in the upper granite had formed before the granite at greater depths had crystallized.

"The formation of aplite and pegmatite dykes may have some connection with these changes. After a considerable proportion of the upper part of the magma had crystallized out, but whilst the remaining lower magma had not changed in composition to any considerable extent, apart from becoming somewhat more acid, relief of pressure along fissures in certain zones would permit this magma to rise into the overlying granite, and, with rapid loss of volatiles consequent upon this relief of pressure, such intruded magma could locally become 'dry' and rapidly crystallize out as aplite. These aplites are usually rather less kaolinized than is the granite.

"The pegmatites belong to a later phase than the aplites, and are more closely connected with the mineral veins themselves. They have been formed from a very late 'wet' magma, in which crystallization would be long-delayed, permitting a coarser-grained texture and the accompaniment of much muscovite. Local pockets of such magma may be left isolated in the consolidated rock and may eventually give rise to pegmatites in the granite; such pegmatites need have no roots and even small tin veins may be formed in this way. Other pegmatites may be derived from magma which has come from depth. It is probable that some of the constituents (such as feldspar and quartz) of these pegmatites were picked up by the liquid in consequence of its reaction on the granite during migration or the liquid may actually recrystallize the granite *in situ.* There is aggradation between some pegmatites and the quartz lodes proper.

"Finally the stage of formation of the mineral veins was reached. There appear to be all stages between the pegmatites and lode quartz, even within some of the veins themselves. Hence the veins must be regarded as representing a final phase immediately following and, in fact, a continuation of the pegmatite intrusions. The residual liquid was obviously extremely high in volatiles and its vapour pressure must have increased enormously in the final stages. Once fissures in the overlying granite tapped this liquid its injection must have been almost instantaneous. The extreme pressure of these liquids would assist in widening the vein walls, even apart from any replacement which may have taken place.

"Following injection, with sudden relief of pressure, the more volatile constituents would tend to escape and react with adjacent minerals of the wall-rock or find their way towards the surface and would thus be entirely lost to the remaining ore liquid. It is noticeable how completely the fluorite and much of the tourmaline was deposited at the beginning of the sequence. It is possible that a considerable part of the H_2O content of the ore liquid also was dispersed after injection. The remaining liquid still contained some B_2O_3 and was obviously high in silica, tin, wolfram, iron, manganese, sulfides, calcium, with also a little beryllium, alumina magnesia, lithia and alkalies,—a liquid which must obviously be alkaline in reaction. The mode of combination of the Sn was certainly not as a fluorite, for all F had now disappeared; it was presumably in the form of SnO_2. The stability of such a liquid cannot be reconciled with a normal solution in which H_2O is the dominant constituent. It may be suggested that, following on the sudden change in composition of this ore liquid after injection and loss of volatiles, the constituents separated out as a dispersed colloid. The prolonged and gradual crystallization from this colloid eventually gave rise to very coarsely crystalline vein minerals, the early sequence of tourmaline, cassiterite, wolfram, beryl and quartz being followed by sulfides and carbonates. There is no evidence and no justification for the assumption that, in these veins, the ore liquid was in constant upward movement, and, apart from loss of water in an upward direction along the lode channel itself as the colloid crystallized, there could have been no great redistribution of material. Shrinkage accompanying crystallization of the colloid, with adjustments along the lode under pressure, would give rise to sufficient mineral fracturing to permit movement of this final water. The last minerals to form, carbonates and scheelite, were probably the results of the reactions of this residual water.

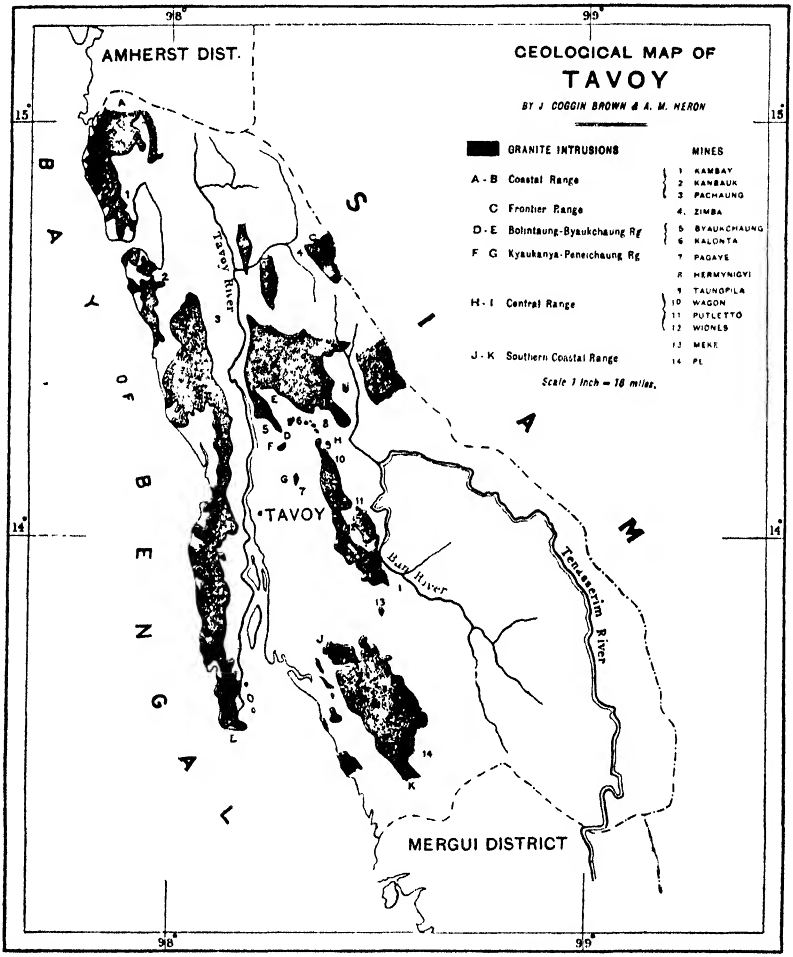
"In the above picture it has been suggested that the ore liquid was injected as a liquid. There is the possibility that, with relief of pressure, the residual magmatic liquid as a whole was injected as a vapour phase which condensed to a liquid in the higher and cooler parts of the granite before deposition, or deposition may even have taken place direct from the vapour phase. Such a process would give rise to a more marked differentiation than is noticeable in these lode minerals, in which volatile and relatively non-volatile constituents are closely associated. Apart from the earliest minerals in the ore sequence, fluorite and tourmaline, which may have been formed as the result of the reaction by F and B_2O_3 vapour given off directly from the injected ore liquid, the rest of the lode materials examined appear to have been deposited from an ore liquid which had not passed through a vapour phase.

"One point which I have endeavoured to bring out is that in these magmas, which contain an abundance of highly volatile constituents, there is not, during crystallization, one single stage which can be referred to as pneumatolytic. The action of these volatile constituents both as vapours and in the liquid phase is continuous right from the moment of intrusion to the final stage of ore deposition. Loss of volatiles, whether it be by mere vaporization or consequent upon phases of ebullition, is a continuous process."

Tavoy[21]

Geology. The predominant rocks of the Tavoy District consist of a presumably pre-Cambrian group of sediments, the Mergui series, comprising argillites, volcanic agglomerates, quartzites, occasional limestones and conglomerates. Granite intrusions into the Mergui series are widespread and are indicated on the map (p. 56).

Modes of occurrence. Wolfram and cassiterite occur in Tavoy as "segregarion deposits in muscovite granite; in pegmatite veins with quartz, feldspar, mica, fluorite, scheelite, molybdenite and sulphides of iron, copper and lead, the last named being rare; in quartz veins with mica (practically always), fluorite (often), molybdenite (sometimes), pyrite (practically always), chalcopyrite (sometimes), pyrrhotite (in some cases), galena (rare), arsenopyrite (rare) zincblende (rare), bismuth (rare), bismuthinite (rare) and topaz (in one case only); in greisens with mica and pyrite. Wolfram and cassiterite occur in residual, detrital, and talus deposit." On the whole, quartz veins furnish the great bulk of concentrates in Tavoy.



Geological map of Tavoy.

In general, the veins strike NNE-SSW and dip highly towards E. The ore-bearing veins appear to be connected only with the upper and outer parts of the granite intrusions. Veins traversing the granite appear to contain larger amounts of cassiterite than those traversing the sedimentaries.

Mines. In the Tavoy district over 100 concessions have been granted to different individuals and companies for mining wolfram ore. Among the mines that have produced sizable quantities of wolfram the following are the most productive, according to J. Coggin Brown and A. M. Heron: (map 56).

Granite Intrusions	Mines
Coastal Range	1. Kambay
	2. Kanbank
	3. Pachaung
Frontier Range	4. Zimba
Bolintaung-Byankchaung Range	5. Byankchaung
	6. Kalonta
Kyaukanya-Peneichaung Range	7. Pagaye
	8. *Hermyingyi*
Central Range	9. Taungpila
	10. Wagon
	11. Putletto
	12. Widnes
Southern Coastal Range	13. Meke
	14. Pe

The most important of the above is Hermyingyi, at which 60 different veins have been worked. These veins have been followed for a distance of from 500 to 1,100 feet and have a width of from 10 inches to 5 feet. They continue upward from the granite into the sedimentary rocks above. Large veins carry from 1.5 to 2.6 per cent WO_3. The proportion of WO_3 to SnO_2 in the concentrates obtained was approximately 2 to 1. Scheelite, arsenopyrite, tourmaline and calcite, which occur in appreciable percentages in the Mawchi ores, are absent here. Fluorite is rather more abundant in the ores from Hermyingyi than in those from Mawchi.

With regard to the process of mineralization of Hermyingyi the following is taken from Dr. J. A. Dunn's paper on "Tin-Tungsten Mineralization at Hermyingyi"[22]:

"The emplacement of these ores in the veins would appear to have been a simple injection of the ore liquid along the vein fissures. The elongated habit of the wolfram, many of the slender crystals projecting from the walls into the coarse quartz towards the centre, at once indicates that there could not have been any important reopening of the fissures prior to deposition of later minerals; whatever crushing of wolfram that did take place was local and probably due to small adjustments during crystallization. The whole aspect of these coarsely crystalline veins is that of a siliceous ore liquid suddenly injected, probably under pressure such as to force the walls apart, and slowly crystallizing from the walls inwards.

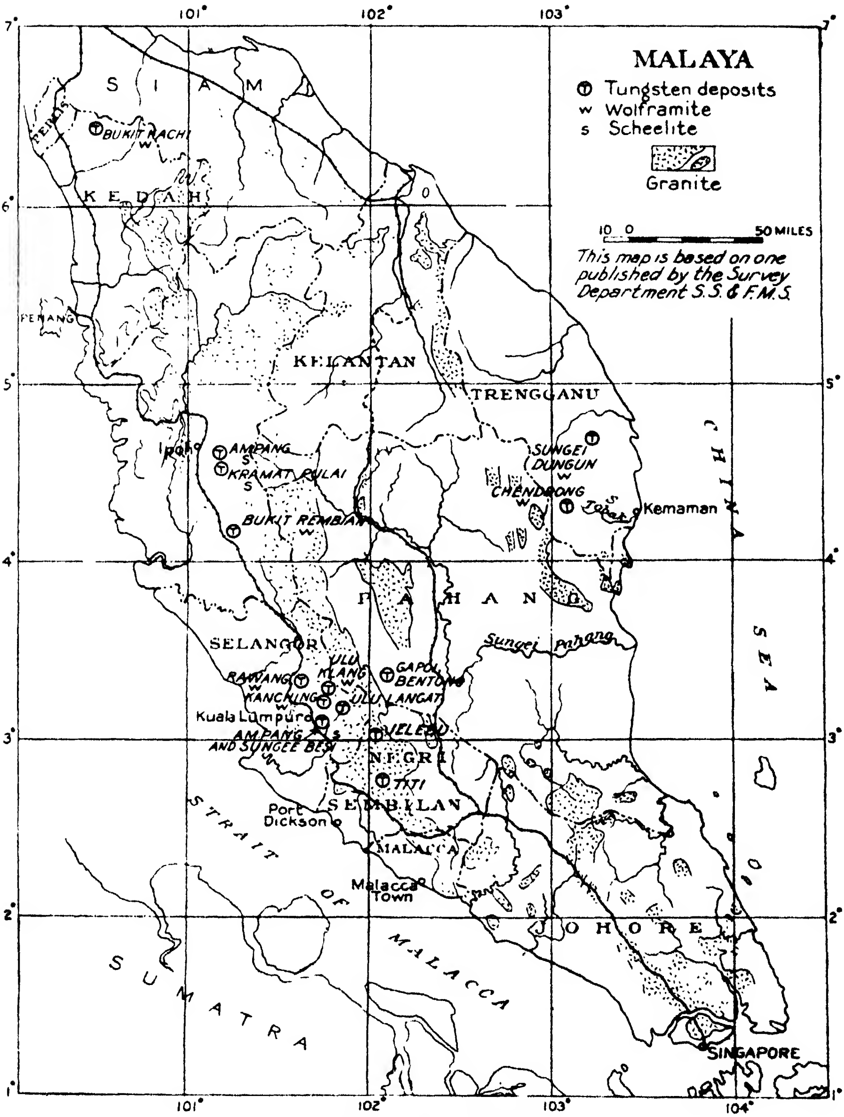
"There is no evidence leading to the assumption that the Sn was injected other than as oxide or the tungsten other than as the wolfram molecule. Fluorite is present in only very small amounts although it is more abundant than in the Mawchi ores, and, apart from prolonging crystallization to a rather lower temperature, fluorine was a relatively unimportant agent in the ore liquid. The total absence of B_2O_3 is remarkable for ores of this nature, and there is not a characteristically high-temperature mineral in the sequence. The ores were deposited at very low temperatures from a liquid which was apparently not acidic, and it is not unlikely that the final state of the ore liquid prior to crystallization was that of a colloid.

"The comparison with the Mawchi ores may be completed, then, with the observation that the Mawchi ores crystallized within a rather wider range of temperature, the earlier minerals being characteristically high-temperature minerals, and the later separating at a much lower temperature. The Hermyingyi ores commenced crystallization at quite a low temperature, probably in consequence of the rather higher amount of fluorite present. At Mawchi, fluorite escaped from the ore liquid at an early stage, at Hermyingyi it was fixed in the fluorite molecule, calcium carbonate being absent. The absence of calcium carbonate is also the explanation of the absence of scheelite from these ores, the wolfram, apparently unstable in the presence of calcium carbonate, remaining unreplaced.

"The quartz-mica-greisen which is so common along the walls of these veins was probably formed by the residual waters, unable to escape fully along the lode channels, soaking into the walls and replacing the feldspars by muscovite. It is illogical to presume that this greisen provides evidence of the very dilute nature of the ore liquid, for the greisen bands are relatively narrow and the amount of water which they represent is relatively small. In my opinion there is no evidence which would suggest that the ore liquids were of such a dilute nature as is usually pictured; deposition from a by no means highly dispersed colloid is a possibility that is in conformity with the little evidence which this study has afforded.

MALAYA

It has already been noted that the Malay Peninsula forms a single geological structural unit. According to Dr. W. R. Jones, the geological features of the mineralized region are essentially as follows: the oldest rocks of this region consist of schists, phyllites, quartzites and slates, together with limestones of Carboniferous or Permo-Carboniferous Age. All of these were invaded and metamosphosed by a tin-wolfram granite, probably during the Mesozoic age.



Tungsten deposits of Malaya.

Scrivenor[23] lists the following localities where tungsten-bearing deposits have been found (unless otherwise noted the tungsten mineral is wolframite):

Kedah: Bukit Kachi Mine
Negri Sembilan: Titi

Perak: Bukit Rembian; Ampang (scheelite) and Kramat Pulai (scheelite)

Selangor: Ulu Klang, Ulu Langat, Ulu Kanching, Ampany, Sungei Besi (scheelite), and Manching near Batu Caves

Trengganu: Dungun and Chendrong

At present the chief producing region is Kramat Pulai, near Ipoh (Perak). Except the scheelite from here, all the tungsten ores carry more or less tin. The deposit at Kramat Pulai is in limestone schists near a contact with granite.

Only small quantities of wolframite amounting to less than a hundred tons per year are mined from the other regions.

THAILAND (SIAM)

It is remarkable that Thailand, although belonging to the same geological structural unit as Lower Burma and the Malay peninsula, is so far comparatively poor in tungsten deposits. Wolfram is mined in the districts of Nakacon Sritamarat, Trang and Lacon.

INDO-CHINA

Wolfram deposits occur as quartz veins cutting both granulitic formation and granite on the flanks of the Pia-Quac Mountain, in the N'Gugen Bim district, in the province of Cao Bang, Tonkin.

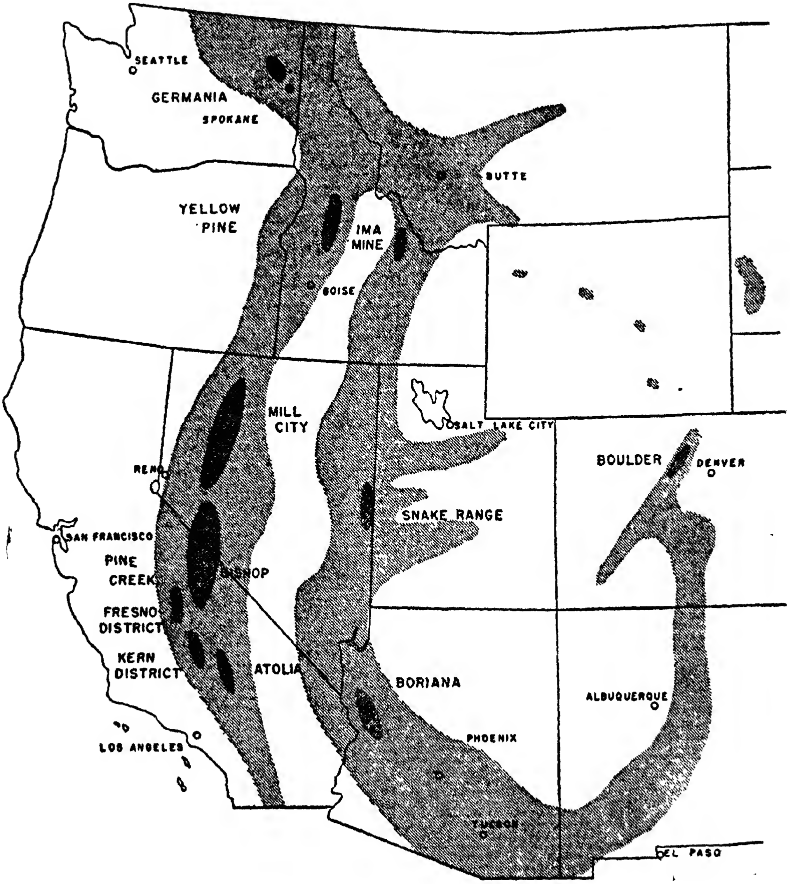
UNITED STATES

Tungsten deposits in the United States lie almost wholly in the area stretching from the Rocky Mountains westward to the Pacific coast. For discussion, this area may be divided into two sub-provinces; namely the Great Basin Sub-province and the Rocky Mountain Sub-province.

East of this area, excepting the important deposit recently discovered in Vance County, North Carolina, to be described later, only three sporadic deposits have yielded any commercial quantities: a small deposit in highly metamorphosed limestone at Trumbull, Connecticut; veins at and in the vicinity of Silvermine, Missouri and a pegmatite at North Groton, New Hampshire, where some wolframite was taken out in the course of mining for mica. The output of each has been insignificant.

Magmatic segregations of tungsten minerals in the United States are uncommon; the only known occurrence of tungsten ores of this form is in the Whetstone Mountains 12 miles east of Benson, Cochise County, Arizona. Contact metasomatic deposits of tungsten are the prevailing types in the Great Basin Region, between the Rocky Mountains and the Sierra Nevada. Although tungsten minerals are not uncommon in pegmatite dikes, yet they do not form any deposits of commercial importance. The vein type of tungsten deposit is also common in the Great Basin and Rocky

Mountain regions and is becoming of great importance in the tungsten production of the United States. Recently, development work at the Yellow Pine Mine and the Ima Mine, both in Idaho, gives indications that these two mines may eventually become the prime producers of tungsten in the United States.



Tungsten-bearing zones in the western states. More productive regions are indicated in darker shade. Important districts are shown by name. *After P. F. Kerr.*

(1) The Great Basin Sub-Province

Between the Rocky Mountains and the Sierra Nevada lies the Great Basin with a large number of deposits whose relationships are with the

Wasatch, the Basin Ranges, and the Sierra Nevada, rather than with the Rocky Mountains.

It is a region over which limestone is widely spread and in which are either a great number of instructions of related granitic rocks, such as quartz monzonite, granodiorite, and others, or a deeply and widely underlying batholith, from which the intrusions are protuberant and are younger than the limestones. A result of the intrusions has been the formation of a large number of tactites, veins and pipes carrying scheelite, a few veins carrying hübnerite, and others carrying wolframite. This area may be arbitrarily considered as running to the crest of the Sierra Nevada on the west and across the Mexican boundary on the south. On the north it is bounded roughly by the state lines of Utah and Nevada.

(a) **California-Nevada Belt Region.** In this belt are found some of the most important tungsten mines in the United States: Mill City (contact metamorphic), Silver Dyke (vein), Nightingale (contact metamorphic), and Oreana (pegmatite), in Nevada; and Atolia (vein), Pine Creek, Tungsten City, Tungstore, Tungsten Hills and Black Rock (all contact metamorphic) in California.

The Great Sierra Batholith, which was intruded near the close of the Jurassic Period, lies along this belt. The smaller areas of granitic rocks bordering it are satellitic to the main batholith and apparently intruded at about the same time. There was also another granitic intrusion in the early Tertiary age. Tungsten deposition apparently accompanied both periods of granitic intrusion.

In this belt tungsten ore has been found in tactites (contact-metamorphic deposits), in pegmatites, and in quartz veins. Each type has furnished tungsten of economic importance, although the contact metamorphic deposits are apparently the most important. The deposits at Mill City, Pine Creek and Atolia have been the outstanding producers in the United States in recent years.

Contact Metamorphic Deposits

The contact metamorphic tungsten deposits are only an extreme variety of the replacement deposits, and the replacing aggregate is known as tactite. Tactite has been adequately described by Hess and Larsen[24]. Here as elsewhere, tactite is found essentially near the contact of limestone with granite or closely related rocks. When igneous rock invades carbonate rocks, the heat and the emanations from molten magma cause a series of changes in the invaded rocks, and also in the invading rock itself, involving solution, formation and deposition of new minerals, and emigration of some old minerals carried on by moving gases or liquids. The solutions naturally follow along cracks or other open spaces in the igneous rock, in the sediments, and between the two; and not uncommonly tabular or less regular bodies thus deposited extend along a certain bed of limestone or along a fracture.

When the solutions happen to carry tungsten it combines with the calcium of the rock and oxygen to form scheelite. Scheelite is indeed the only tungsten-bearing mineral found in the tactite in Nevada and California. Garnet, epidote, quartz, and calcite are the most common minerals associated with scheelite in this type of deposit, with diopside, hornblende, chlorite, actionolite, and mica next in abundance. The following minerals have also been reported: vesuvianite (Queens), fluorite (Queens), laumontite (Nightingale), halloysite (Ragged Top), apatite (Golconda), titanite (Golconda), and clinozoisite (Toy). Pyrite and chalcopyrite are the common metallic minerals found in tactite; occasionally molybdenite, bismuth (Ruby Range), bismuthinite (Ruby Range), galena (Pilot Mountains), and magnetite (Humboldt Range) have also been reported.

Veins. Tungsten-bearing quartz veins have been found in Snake Range, Round Mountain, Paradise Range, Tonopah, Silver Dyke, and Atolia. It is significant to note that when the quartz veins occur in the carbonate rocks, the tungsten-mineral is invariably scheelite (Osceola, Snake, Sacramento, Shoshone, Cherry Creek, Paradise Range), while the tungsten mineral in the veins cutting granite or closely related rocks is usually hübnerite (Tungsten, Tungstonia, Cherry Creek, Round Mountain). Cherry Creek deposits furnish a good example. Here quartz veins occur both in limestone and quartz-monzonite. In the former, the vein carries scheelite; in the latter, the tungsten mineral is hübnerite. In the Silver Dyke Mine diorite occurs as wall-rock and vein breccia. No limestone occurs, yet the tungsten mineral is scheelite. It is found, however, that the diorite here contains 5 to 7 per cent of CaO. In the Tonopah district, where the gold-silver veins cut a complex volcanic series, small amounts of both scheelite and hübnerite have been found.

Quartz is the most common gangue mineral either in scheelite veins or in hübnerite veins. Fluorite seems to be especially associated with hübnerite veins and has been found in Tungsten, Tungstonia, and Round Mountain deposits. Triplite (Tungstonia) and muscovite (Round Mountain) have also been reported. In the scheelite vein of Paradise Range, gangue minerals include quartz, vesuvianite, epidote, rutile, tremolite, apatite, serpentine, and leuchtenbergite. The chief gangue minerals of Silver Dyke are quartz and albite. In the Tonopah vein, quartz, sericite and adularia are the common gangue minerals. Metallic minerals found occasionally in the tungsten-bearing quartz veins include pyrite, chalcopyrite, pyrrhotite, galena, sphalerite, bismuthinite, gold, silver, argentite, polybasite, and tetrahedrite.

Pegmatite. Throughout the Nevada Region, tungsten-bearing pegmatites are of rare occurrence, and no very large pegmatitic tungsten deposits have been known all over the world. The Oreana tungsten deposit in the Humboldt Range, however, is considered pegmatitic. The chief minerals here are beryl, oligoclase, albite, quartz, phlogopite, fluorite, and scheelite. The deposit occurs both in dikes and in lens along the limestone-metadiorite contact.

Mill City[25] (Nevada). The tungsten deposits are located at the mining camp called Tungsten, 5000 feet above the sea level on the eastern slope of the Eugene Mountains, eight miles west of Mill City.

The area is composed of two principal units, a metamorphosed sedimentary series consisting of hornfels, argillite, phyllite, limestone, and quartzite, and an intrusive granodiorite. The sedimentary series is separated by the Stank fault extending in an almost N-S direction into two groups. East of the fault, contact metamorphism has been active, and the limestone beds have been largely replaced. These contain the principal high-grade ore. The beds vary from 3 to 15 feet in thickness.

The ore bodies are vein-like in form but have been produced by contact-metamorphism of thin limestone members, in the silicified argillaceous sedimentary series. Extreme deformation, faulting, and fracturing have separated the ore bodies into isolated nearly vertical sediments arranged *en echelon* along a bearing of about N 20° E.

The normal ore contains about 1.10 per cent of scheelite, while the concentrates average 75 per cent WO_3. The ore consists of fine grained scheelite disseminated through a ground mass consisting largely of garnet, epidote, quartz, and calcite, with scattered crystals of pyrite.

Silver Dyke[26] (Nevada). The district is in the Excelsior Mountains in southern Mineral County. A four and one-half mile vein system extending across the northern end of the Excelsior Mountains is commonly referred to as the Great Silver Dyke of western Nevada. It is reported that the Silver Dyke deposit is practically exhausted, and the mine is abandoned.

The core of the Excelsior Range in the vicinity of Silver Dyke is intrusive diorite. A great thickness of old volcanics with some intercalated sediments have been invaded by the diorite in the vicinity of the tungsten-bearing veins. The vein system truncates the diorite. Both west and east of the exposed mass of diorite, the vein system penetrates a cap of younger lavas which forms a broad belt on either side of the range. It is believed that the older volcanics are Triassic, the younger Tertiary, and the diorite is probably a phase of the post-Jurassic intrusion of western Nevada.

The vein system is remarkably uniform and continuous in an east-west direction. The maximum width of the vein system proper is about 200 feet, but in places it is not more than 25 feet. The quartz types recognized as part of the vein system are five: ribbon quartz veins, replacement series, stringer zone, cemented breccia, and sheared quartz. Of these five, the replacement quartz zone is the principal ore-bearing zone. It is normally about 4 feet in width, but in the highly mineralized portions of the workings, it is at least 15 feet thick. Approximately two-thirds of this area normally carries scheelite. It is believed that the scheelite has been formed by the reaction of tungsten-bearing solutions of the veins with the calcium of the diorite which occurs as wall-rock and vein breccia. The diorite contains from 5 to 7 per cent of CaO.

The chief vein-forming minerals of Silver Dyke are quartz, albite, and scheelite. Kaolinite is present, but appears to represent a late vein filling. Other minerals occur in minor amount.

Oreana[27] (Nevada). The deposit is located along the western margin of the Humboldt Range. Lovelock is about twenty miles to the southwest. The deposit is said to be now approaching exhaustion.

The oldest rocks in the Humboldt Range are the kerotophyre and rhyolite tuffs, flows, and breccias, exposed on both sides of the range. Outcrops on the west side occur both to the northeast and southeast of the Oreana tungsten deposit, but are not found in the immediate vicinity. Uncomformably overlying these volcanics is the so-called Star Peak formation which consists of limestones and siliceous and tuffaceous beds of Middle and Upper Triassic age. These have been intruded by metadiorite, early aplite, granite porphyry, granite, aplite-pegmatite dikes, and diabase, believed to have originated in the order named.

Pegmatite dikes cut the metadiorite and also the granite. These occur in the tungsten area, where invading metadiorite may carry high-grade scheelite. The solutions responsible for contributing the pegmatite appear to have migrated upward in places through the limestone, but chiefly along the contact between the metadiorite and the limestone. The best indication of the latter feature is furnished by the existence of the ore bodies along the contact. These ore bodies form rounded lenses at the contact and rest upon the limestone.

The Oreana ore is unique among American tungsten deposits in that the scheelite mineralization is considered pegmatitic. One stretch of nearly 100 feet, where mining started, yielded scheelite ore suitable for shipping without concentration, after hand sorting. It is the high grade of ore that merits exploitation. The first ore shipped contained about 30 per cent scheelite. Since that time, a considerable tonnage of ore in lenses along the limestone-metadiorite contact, averaging about 5 per cent scheelite, has been removed.

Two forms of scheelite deposition occur: (a) in complex pegmatite dikes that cut metadiorite; (b) in lens-like masses along an inclined contact between limestone and metadiorite. Minerals associated with scheelite include beryl, oligoclase, albite, and phlogopite. Fluorite and quartz form adjacent masses. Garnet and epidote are virtually absent.

Zones of silicification and alteration lead downward from the limestone-metadiorite contact within the limestone, but contain only traces of scheelite. It is believed that such zones represent channelways leading to ore deposition above and are pegmatitic in character. The siliceous metadiorite has been shown by field occurrence to be a more favorable host rock than the limestone.

Golconda (Nevada). The tungsten deposit at Golconda, as described by Prof. P. F. Kerr[44] is both interesting and unique. It is a tungsten-bearing psilomelane deposit, the tungsten content, WO_3, being in colloidal condition, and varying from about 1 to 7 per cent. Analyses show that the material consists essentially of manganese, barium, potassium, and tungsten oxides with water, for which Kerr proposes the name *tungomelane*. Treatment of this ore is described on p. 168.

The tungsten-bearing manganese deposits lie blanket-like on an erosion surface and underlie beds of calcareous tufa. "The tungsten-bearing blanket deposit varies from a few inches to several feet in thickness and is best exposed in the crescent-shaped rims which crop out around upper margins of the tufa caps. Beneath the blanket deposits are veins of similar mineralization which are thought to have provided the source of the overlying ores."

Atolia[28] (California). The Atolia mining district lies near the northern edge of the Mojave Desert, in San Bernardino and Kern counties. Here are found many gold-bearing veins which were the source of much of the gold in the Atolia placers. The rock that contains the scheelite veins is quartz monzonite, probably of late Jurassic origin.

"The tungsten-bearing fissure veins at Atolia contain the largest bodies of high-grade scheelite discovered in the United States and possibly in the world". These veins are fissure fillings with little replacement of the country rock. The gangue consists of quartz, carbonates (calcite, ankerite, dolomite, and siderite), and sporadic pyrite, stibnite, and cinnabar. The scheelite veins may or may not contain gold, while some other veins are gold-bearing but carry no scheelite. The largest ore shoot discovered, that in the south vein of the Union mine, has a vertical distance of 850 feet and a breadth of 1,260 feet. The thickness of ore mined by the companies has ranged from a few inches to 17 feet. At present the grade of ore milled is about 2 per cent WO_3.

"The alluvium that blankets the Atolia district contains a large quantity of scheelite. . . . Although the scheelite content of the alluvium is very uneven and over much of the district is too small for profitable extraction at any probable peacetime prices, the presence of placer gold in relatively large quantities may make it possible to extract tungsten as a by-product".

Past production indicates that the district contains large quantities of alluvium which carry 1 to 1.5 pounds of scheelite per cubic yard. Probably all the placer area may yield on an average one-fourth pound of scheelite per cubic yard, besides some gold. It is said that the lowest gold value found in prospecting between the Stringer district and Cuddeback Lake is $0.35 per cubic yard.

Pine Creek[29] (California). The Pine Creek Co., of Bishop, has a large tactite body near the crest of the Sierra Nevada. The greater part of the mountains about the deposit is made up of granitic rock which surrounds the sediments, mostly of quartzites, schists and marble.

"The tactite is for the most part a rather dark green medium-grained rock, made up chiefly of red-brown garnet and dark-green diopside-hedenbergite, with more or less fluorite, apatite, and titanite. Several periods of metamorphism are clearly shown in this deposit. After the garnet-diopside rock was formed it was shattered, and the fractures were healed by a feldspar-vesuvianite rock; later quartz lenses, carrying scheelite, were deposited; and still later the sulfides pyrite, chalcopyrite, and molybdenite were deposited along fractures associated with alteration of diopside-hedenbergite to quartz and calcite. Veinlets of prehnite and epidote, lenses of coarsely crystalline calcite associated with sulfides, and a large body of laumontite appear to represent late periods in the metamorphism.

"Data are not available for an accurate estimate, but a rough approximation is about half a million tons of tactite for each 100 feet of depth. Not all of this material is ore, but sampling by the operators indicates that a considerable part pans well in scheelite and samples carefully tested by engineers for the company over 15-foot squares to cover the large body at the south end of the deposit are said to have run from 0.5 to 1.5 per cent and rarely up to 5 per cent of WO_3, and to have averaged a little over 1 per cent."

Tungsten Hills[30] (California). The Tungsten Hills lie at the base of the Sierra Nevada, 10 miles west of Bishop.

"The Tungsten Hills are composed dominantly of granite and quartz diorite, which enclose small masses or roof pendants made up of metamorphic rocks that are older than the granite.

"The pendants are composed of metamorphosed sedimentary rocks that were originally shale, sandstone, and limestone but were changed by the intrusion of the granitic rocks to schist, hornfels, quartzite, skarn or tactite, and marble. The shale was altered to hornfels and mica and andalusite schists. Sandstone, depending upon its composition, became quartzite or quartz-mica schist. The calcareous rocks, limestone, shaly limestone, and calcareous shale, show the most varied alteration. Some beds are silicified and on casual inspection resemble quartzite; others, which were probably nearly pure limestone, have been re-crystallized to marble; and some of the thin-bedded shaly limestone has become a spotted tactite and now consists of interlayered silicated and silicified limestone. Some beds are composed essentially of granular vesuvianite, whereas others have been entirely altered to a coarsely crystalline rock known as "tactite", composed of variable amounts of garnet, epidote, diopside, amphibole, calcite, and quartz, which are usually accompanied by minute quantities of scheelite, apatite, sphene, and sulfides.

"Tungsten deposits are confined to the calcareous beds in the pendants and are restricted in large part to the portions of the calcareous beds that have been altered to tactite. Not all the tactite, however, contains tungsten, the ore occurring sporadically in bunches even in the favorable beds.

"Past production records indicate that on the average slightly over 0.5 per cent of WO_3 has been recovered from the ore mined, although large specimens containing as much as 10 per cent of WO_3 have been found locally."

Tonnage of probable ore has been estimated to be 100,000 tons, the grade of which may average between 0.25 and 0.5 per cent WO_3.

(b) **Utah.** In Utah tactite deposits in Box Elder County 15 miles northeast of Lucin produced some scheelite during the Great War. Near Gold Hill in the Deep Creek Mountains, pipes in quartz monzonite yielded some scheelite, and 40 miles south near Trout Creek are scheelite-bearing veins of small size. Scheelite ore has been mined near Milford, Beaver County. On the whole, the tungsten deposits in Utah do not appear to be promising.

(c) **Arizona.**[31] Most of the tungsten mines are widely located in a NW-SE belt running diagonally across the state, including the counties of Mohave, Yavapai, Maricopa, Pinal, Pima and Cochise.

Most of Arizona's tungsten production has come from lode deposits. A few places, as in the Little Dragon (Cochise County) and Camp Wood (Yavapai County) areas, for example, have yielded notable amounts.

The lodes occur in metamorphic or sedimentary rocks, invaded by granite, granodiorite or pegmatite presumably of the Mesozoic-Tertiary age. Gangue and associated minerals may include the following: quartz, calcite, dolomite, ankerite, siderite, feldspar, muscovite, chlorite, tourmaline, topaz, fluorspar, hematite, copper carbonates, pyrite, chalcopyrite, chalcocite, galena, molybdenite, stibnite, arsenopyrite, silver minerals, gold, bismuth, columbium and tantalum minerals and (rarely) cinnabar.

Boriana Mine is situated in the Hualpai Mountains, Mohave County. During 1933–37, this mine was the "leading tungsten producer in Arizona and probably the second in the United States: for the 2-year period, 1936–37 its output averaged about 3000 tons per month." The quartz veins in general strike N 30° to 40° E and dip from 75° SE to vertically, paralleling the schist in which they occur. "As exposed in the mine, the veins are lodes of composite type, made up of two to ten or even twenty parallel quartz veins and stringers, separated by schist, within widths of a few feet to 20 or more feet. Many of them consist of two veins from 4 to 10 inches, or exceptionally 4 feet, wide with narrower veins or stringers in schist between. At least four of the composite lodes have been encountered in the mine within a width of 200 feet."

The ore minerals consist of wolframite, scheelite, and chalcopyrite, together with hematite and a little gold and silver. The gangue is principally quartz with minor amounts of calcite and fluorite. The ore averages 1.45 per cent WO_3 and 0.75 per cent copper.

Besides the Boriana Mine, there are more than thirty tungsten deposits in Arizona, of which the most important are Camp Wood (Yavapai County) Las Guijas (Pima County) and Huachuca Mountains (Cochise County).

(d) **Oregon.** A little scheelite has been reported from the Cliff Mine, near Sumpter. Scheelite-bearing tactite carrying molybdenite also is known 18 miles south of Joseph, Wallowa County, Oregon, and as other tactite masses are known in adjoining parts of Oregon and Idaho, more may be found to carry scheelite.

2. The Rocky Mountain Sub-Province

(a) **Boulder County**[32] (Colorado). The principal group of tungsten deposits in the Rocky Mountain area lies around Nederland and between Nederland and Boulder, in Boulder County, Colorado. Before the First World War it was one of the richest fields known. The tungsten mineral is ferberite ($FeWO_4$), which occurs in veins most of which have proved to be small with rich shoots of ore here and there. The field passed its zenith between 1914 and 1918, and since then production has required a greater and greater effort.

Veins of ferberite occur in pre-Cambrian gneissic quartz monzonite. The veins are largely made up of a very fine-grained quartz called "horn rock," through which the ferberite is distributed. Much of the mineral is in very small grains, some of which are less than 0.002 inch in diameter. Concentration is therefore difficult and concentrates may carry less than 50 per cent WO_3—those made from the Wolf Tongue Mining Company's ores carry between 30 and 58 per cent WO_3.

The minor constituents of the veins, named in approximate order of deposition, include hematite, magnetite, fluorite, dickite, ankerite, siderite, barite, pyrite, marcasite, calcite, galena, sphalerite, freibergite, tetrahedrite, miargyrite, adularia, montmorillonite, halloysite, beidellite, scheelite, and opal.

The width of the veins ranges from 6 inches to 3 feet, but in places ore bodies from 12 to 16 feet wide have been exploited. The grade of ore as mined commonly ranges from 2 to 20 per cent WO_3.

The veins of the Boulder field do not extend to very great depths; little ore has been found below 300 feet from the surface, though in one mine, the Conger, a little was found at a depth of 650 feet.

Concerning the origin of the deposits, T. S. Lovering writes: "The argilliferous altered rock bordering the veins indicates attack by acid solutions, and the narrow inner sericitized casing shows a change to neutral and alkaline solutions at a later stage. Within the veins the formation of dickite and marcasite immediately preceded the deposition of pyrite and ferberite. Hypogene brown iron hydroxide was formed later than the ferberite, and barite and adularia later still. This sequence indicates a progressive change from acid to alkaline solutions and harmonizes with the evidence of wall-rock alteration. Ferberite was apparently precipitated in very slightly acid solutions. Sphalerite, galena, tetrahedrite, chalcopyrite, and miargyrite are later than the ferberite and brown iron hydroxide and were presumably precipitated in alkaline solutions.

"Field evidence suggests that the source was a biotite-latite magma heavily charged with volatiles. It is suggested that emanations from the underlying latite magma rose through the hot porous explosion breccia with little change in character, that by reaction with the monzonitic wall-rock of fissures higher up they became neutralized and finally alkaline through the acquisition of bases, and then deposited their loads in these fissures. It seems probable that the deposits were formed at temperatures between 200° and 300° and under pressures of not much more than 100 atmospheres."

(b) **Idaho.** It is probable that the Yellow Pine Mine, located in the northeastern part of the Yellow Pine district, in Valley County of central Idaho, may eventually, with further development, become the largest tungsten producer in the United States.* It has been worked for many years as a gold and antimony mine and it was only in the early part of 1941 that scheelite was discovered. It is reported that about 30,000 units of tungsten as WO_3 can be produced per month. The prevailing formation is quartz monzonite. The scheelite ore body occurs in a shear zone in the

---

* It is reported that the scheelite ore body, which was very productive during world War II, has been substantially mined out.

form of a V, the western side of which is marked by a lamprophyre dikes while the eastern right side is the Meadow Creek fault. The ore mineral, in the ore zone are stibnite, scheelite, gold and silver. The principal associated sulfide minerals are pyrite and arsenopyrite. The main body of tungsten ore contains: 3–4 per cent WO_3, about 5 per cent antimony, 0.08 ounce of gold per ton, and a minor amount of silver. The distinguishing feature of this deposit is that the scheelite mineral acted as a binding agent, cementing the breccia fragments in the shear zone. Mecia named this type of scheelite deposit, the "breccia" type. According to Mecia, "The occurrence of most of the scheelite in breccia zones suggests that there was brecciation, possibly by fault movements following the gold-arsenopyrite-pyrite deposition, and that the entry of scheelite cemented the breccia fragments. Introduction of the pyrite, arsenopyrite, and gold was probably the earliest mineralization, possibly arriving in two or more surges of mineralization, both being end stages in the emplacement of the Idaho batholith. The gold-bearing solutions evidently arose along the Meadow Creek fault until they encountered the Yellow Pine shear zone and the gold was localized there. The tungsten-bearing solutions also evidently arose along the Meadow Creek fault until they encountered the zone of N 80° E fractures and precipitated scheelite along it. The antimony-bearing solutions probably arose along the same zone and stibnite was deposited in small fractures without control by major structures except the lamprophyre dike on the west and the dacite dike on the east."

The Blue Wing area, in Lemhi County, is another tungsten-mining district in the state, in which the principal producer is the Ima Mine. No igneous rocks are exposed in the Blue Wing district, but granite has been reached in the workings of the Ima Mine. The sedimentary rocks in the district consist of metamorphosed feldspathic sandstones and shales.

"The Blue Wing district contains a complex system of quartz veins, many of which are small and lenticular. Exploration has shown that a few of these, grouped close to the borders of the granite, are relatively large. At greater distance from the granite the veins are more numerous but much smaller and less continuous. The original complexity of the vein system has been somewhat increased by minor postmineral faults."

The principal metal-bearing minerals in the veins are hübnerite, pyrite, silver-bearing tetrahedrite, chalcopyrite, bornite, galena, sphalerite, molybdenite and scheelite; the principal gangue minerals are fluorite, orthoclase, rhodochrosite, mica and talc.

All the known ore shoots are in the larger veins of the Ima Mine. Those on the main level are all in a stretch that extends 1,200 feet from the K. C. Li tunnel junction to the last ore shoot in the granite. The mill heads of the Ima Mine have averaged 0.55 per cent WO_3, or very roughly 0.72 per cent of hübnerite.

Scheelite was found in gold veins at Warren many years ago, but none was produced; it is also found in quartz veins on Tungsten Mountain, 5 miles east of Copeland, Boundary County. In 1916 a little scheelite was mined at Murray, where it occurred with lead and gold in the Golden Chest Mine; in the Winnie May (Friday group) and Mother Lode claims on Pritchard Creek; and on Pony Gulch.

A little ferberite has been mined on Corral Creek, Soldier Mountain, Blaine County, and wolframite has been found on Granite Mountain, near Martin, Butte County

(c) **Montana.** In the Rocky Mountains of Montana hübnerite has been found in small quantity in the Birdie Mine, just northeast of Butte; in several of the copper veins at Butte; at Pony; and near Anaconda. The production has been negligible.

A few carloads of scheelite have been mined at Jardine with gold and arsenopyrite from quartz veins, and unsuccessful attempts have been made to mine it at Crevice, 5 miles southeast; a little scheelite was produced at Libby; and it has recently been found in the Midas Mine, about 36 miles southeast of Libby, but not in profitable quantity.

(d) **Washington.** On the western side of the Rocky Mountains in Washington, wolframite has been found in veins and in greisen on Grouse Mountain, near Deer Park; at Deer Trail (9 miles southeast of Fruitland); and 16 miles west of Addy. A small production has been made from all these deposits; that at Deer Trail, which carries also a little scheelite and bismuthinite, was worked by Tungsten Producers, Inc.

A little scheelite has been found at Lead Point a few miles southeast of Northport, and at Goose Prairie, in northern Yakima County.

During the First World War wolframite-quartz veins, 3 miles east of Cathedral Peak, Okanogan County, were worked somewhat. They are 35 miles by trail west-northwest of Loomis, and a mile south of the Canadian boundary. The principal vein is nearly flat and the enclosing granite is jointed in just such a way as to form walls, roof and floor for a drift. The vein is in places more than a foot thick and at other places pinches. It would probably make a small production at a continued price of $18 or more per unit.

(e) **New Mexico.** In New Mexico a little wolframite has been found on the mountain southeast of Elizabethtown; on Willow Creek on the opposite side of the mountain, and near Penasco, all in Taos County. Some wolframite was mined during 1917 near Gage, Luna County, and a small quantity of hübnerite was mined from rich pockets near the surface at Whiteoaks, Lincoln County. Here the hübnerite veins were closely connected with gold veins and some hübnerite was found at a depth of about 1,350 feet in the shaft, probably about 1,150 feet vertically, but nothing of consequence was found below 75 or 100 feet. A little scheelite was found in a vein on Monte Saolitario, northwest of Las Vegas, and some has been found in tactite near Hachita.

(f) **South Dakota.** There are two main deposits, one adjoining the Homestake gold mine, and the other 2½ miles south of Lead at the Wasp No. 2 gold mine. Wolframite brought up by hot waters replaced a comparatively flat-lying dolomite in both places and the ore carried some gold. The deposits probably yielded between one and two thousand tons of tungsten ore and apparently they are now exhausted.

Hübnerite has been found in small quantity in Two-Bit Gulch, 2 miles southeast of Deadwood. Wolframite occurs with cassiterite (tin oxide) in 3 or 4 quartz veins north of Hill City, 50–55 miles south of Deadwood; in several quartz veins east and southeast; and in several pegmatite dikes. A few tons of ore have been extracted from the veins, but the pegmatites have produced none.

(g) **Alaska.** A few small deposits of scheelite have been found in Alaska; placer scheelite has been found at Nome and at the east end of Norton Sound, and a little placer wolframite in Deadwood Creek near Circle. Scheelite has been found in the valley of Gilmore Creek 15 miles north of Fairbanks, in what are probably replacement deposits. Although a few tons of concentrates was produced during the First World War, no deposits of consequence have been found. Recently tungsten deposits have been discovered in the Hyder and Mayo districts.

3. The Atlantic Coast Region

In Vance County, North Carolina[54], there has been recently discovered a tungsten deposit, which has possibilities, according to the Bureau of Mines, of becoming as important as that discovered in Idaho. "The vein distribution is apparently controlled by a granite-gneiss schist contact and schist septums occurring in the granite. Tungsten deposits have been identified over an area measuring approximately 10 miles along the contact and 1 mile across it. The minerals (hübnerite and scheelite) occur in quartz veins varying in width from 10 inches to 30 feet and having diverse orientations." The associated minerals are rhodochrosite, fluorite, sericite, galena, sphalerite, pyrite and chalcopyrite. It has been proved that there are 300,000 tons of ore averaging 0.96 per cent of WO_3 in sight.

MEXICO

Tungsten is found spasmodically in almost every district in the State of Sonora and the northern portion of the territory of Lower California; but the most notable occurrences are in the following districts.

(a) **Altar District, Sonora.** Of all the prospects now being worked for tungsten, the most important one is the El Tungsteno Prospect. From the several strong parallel quartz veins carrying spotty showings of hübnerite is produced about half a ton of low-grade concentrate per month.

(b) **La Dura-San Nicolas District, Sonora.** This district is by far the most important area of small, scattered miscellaneous production. The country rock is a granite, and the tungsten occurs as scheelite in quartz veins. It has in the past furnished almost all the Sonora tungsten production.

(c) **Santo Domingo Mine, Nacozari, Sonora.** This mine has been operated for a number of years for copper, gold and silver, and it was only recently that the ore was found to carry wolframite also.

(d) **Sierra Pinta Mine, Sonora.** This mine has been operated as a gold mine and it was only recently that scheelite was found associated with the gold ore.

(e) **El Fenomeno Mine, Essenda, Lower California.** Apparently the most important of the mines so far opened in Mexico for tungsten production is the El Fenomeno Mine. Here scheelite is found to occur along the contact between limestone and granite. It is reported that as soon as the renovated dressing plant is in full operation, an annual production of about 500 tons of 60 per cent WO_3 concentrate is expected.

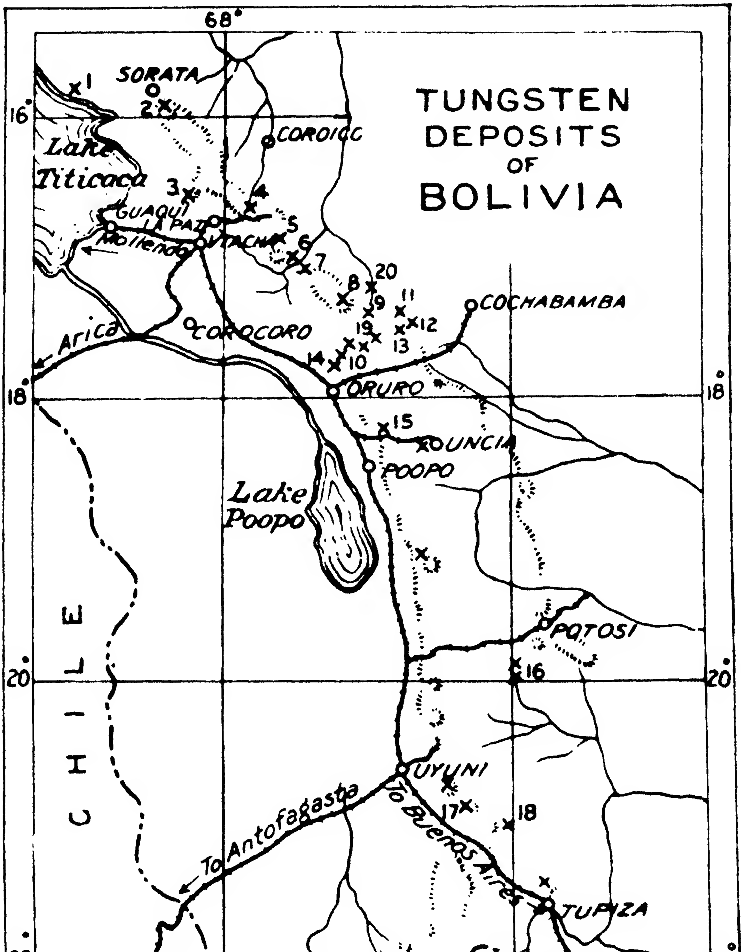
BOLIVIA[33, 34]

"The tungsten ores are formed throughout the tin belt, usually in separate deposits and rarely associated with the tin ores. The principal mines are in the Department of La Paz, with smaller producers in the Departments of Oruro and Cochabamba (and Potosi). The ore deposits occur in the metamorphosed quartzites, usually in fissures normal to the contacts of the granite intrusives, as at the Chojlla and the Araca mines. In some instances the deposits are parallel to the bedding planes of the sedimentaries, as at the Bolsa Negra mine, but they rarely occur within the granite intrusive. Wolframite is the most common mineral, although scheelite is also prominent in some of the deposits. These minerals occur in the vein deposits with quartz alone or associated with pyrite, arsenopyrite, and chalcopyrite, and occasionally with cassiterite. There are also brecciated deposits in the form of irregular lodes in quartzites in which scheelite occurs in the matrix or cementing material, as at the Juliana mine in the province of Oruro. In general, both the geological features and mode of occurrence of the tungsten deposits are similar to those of the tin deposits."

(a) Department of La Paz

1. The Mercedes Mine, 7 miles south of Sorata. The average width of the main vein is about 16 inches. The ore is said to contain 2 to 4 per cent WO_3, 5 to 10 per cent copper and about 1 per cent bismuth.

2. The Susana Mine, 4 miles east of Millapaya. The principal vein is a fissure filled with brecciated quartzite, quartz, arsenopyrite, pyrite and



Tungsten deposits of Bolivia. *1.* Ancoraimes (huebnerite). *2.* Illampu district. *3.* Chacaltaya. *4.* Ungas district. *5.* Mururata district—Taquesa. *6.* Illimani district. *7.* Saya district—Araca. *8.* Pacuni. *9.* Vela Cruz. *10.* San Antonio (ferberite). *11.* Amutara. *12.* Chicote. *13.* Kami. *14.* Conde Auque (scheelite). *15.* Huanuni. *16.* Yura district (ferberite)—Monte Cristo and Colpa Mines. *17.* Tasna. *18.* Leque Palca. *19.* Chorolque. *20.* Quime. *Adapted from F. Ahfeld, Revista Minera de Bolivia, Ano 2, 1927, p. 230.*

some chalcopyrite and it contains from 1 to 4 per cent WO_3. It ranges from 1 to 3 feet in width, the ore occurring in irregular masses.

3. The Hucamarini Mine, 3 miles below the Mercedes Mine. Here three veins have been developed; the upper vein, which is the richest in tungsten, averages a foot wide; the middle vein is the widest and richest in copper and averages over 2 feet in width; in the lowest vein are concentrations of bismutite, together with chalcopyrite, pyrite and arsenopyrite. Average ore mined from these three veins contains 2 to 4 per cent WO_3, 2 to 5 per cent bismuth, and 6 to 10 per cent copper. The chalcopyrite is said to contain 4 grams gold and 250 grams silver per ton.

4. The Chojlla, Enramada and Santa Ana Mines, near Yanacachi, in Sur Yungas. The principal deposits are pegmatitic quartz veins averaging 3 feet in width, with wolframite, some of which contain cassiterite, besides a few with only cassiterite. These occur in quartzites and metamorphosed slates with a general strike parallel to the enclosing rock beds but dipping about at right angles toward the underlying granite intrusive mass. The mineral zone extends over an area 2 miles by 1. The main vein, No. 4, has been developed over a length of 1,500 feet, averages 4 feet in width, and contains 2.5 per cent WO_3 and 1.5 per cent tin. The vein in the Euramada Mine contains only wolframite, with quartz and some sulfides, and it averages about 2 feet in width with 1.5 per cent WO_3.

5. The Liliana Mine, north of Yanacachi. Here veins containing wolframite of the same type as at Chojlla occur.

6. The Aceromarca Mine, southwest of the Liliana. The deposits are quartz veins with wolframite in the Tagneşi granite mass, which vary from 4 inches to 4 feet in width and average about 2 per cent WO_3.

7. The Bolsa Negra Mine, 40 miles southeast of La Paz. This mine is of particular interest because the deposit consists of a number of horizontal veins following the bedding planes of a series of siliceous slates 160 feet thick and developed over a length of 1,000 feet. Within this series, the minable beds of ore, from 2 to 10 inches in thickness and averaging 2.5 WO_3, constitute 15 per cent of the series. The mineralization in these interbedded veins is of quartz containing aggregates of pyrite, wolframite, and scheelite with small amounts of barite and some sphalerite.

8. The Cerro Negro Mine, in the southern part of Sur Yungas. The veins occur in metamorphosed slates and quartzites. Some of the veins contain only wolframite in the quartz feldspathic gangue, while in others the wolframite ore is mixed with cassiterite and sulfides.

9. The Araca Mine, in Quimsa Cruz. Here, besides the tin veins, there are 7 veins with wolframite on the west contact of the Quimsa Cruz granite mass. These veins are 10 inches to 5 feet in width and traverse the granite. The ore mined averages 4 per cent WO_3, the accompanying minerals being quartz and arsenopyrite.

10. The Pacumi Mine, 16 miles northwest of Quimsa Cruz and 75 miles southeast of La Paz, in the province of Inquisivi. The tungsten deposit consists of veins of quartz up to 2 feet in width with both wolframite and cassiterite, occurs in granite near the contact of the Quimsa Cruz granite intrusive. The Veta Blanca, at 15,500 feet altitude, is the most important vein thus far developed. It is a replacement vein 2 to 3 feet thick in quartz monzonite near the edge of the mass. The vein carries wolframite, scheelite (black from enclosed wolframite particles), prochlorite, apatite, pyrite, some chalcopyrite, a little magnetite and tourmaline. The ore mined is said to have averaged 8 per cent WO_3.

11. The Amutara Mine, in the province of Inquisivi. Here a number of quartz veins containing wolframite and arsenopyrite occur in the much-faulted Devonian slates on the east side of Amutara mountain. They are up to a few feet in width, and the ore averages about 2 per cent WO_3.

12. The Pajchiri Mine, on the south side of Amutara mountain. The deposit here is of the same type as that of the Amutara Mine.

13. The Chicoto Mine, in the province of Inquisivi. Wolframite occurs in narrow quartz veins up to 2 feet in width in the metamorphic quartzites and in the hornfels on the northeast side of the Chicote Grande Mountain. The ore ranges from 1 to 5 per cent WO_3 and contains arsenopyrite, pyrrhotite, some chalcopyrite and siderite.

14. The La Perfeccionada Mine, on the west side of the Ayopaya River. This deposit consists of a large rock slide said to contain 3 million tons of low-grade ore with 0.1 to 0.2 per cent WO_3 which might be exploited on a large scale. The ore is wolframite in veinlets throughout the quartzite rock fragments and masses.

15. The Taminavi Mine, on the east side of the Ayopayo River northeast of La Perfeccionada. Here, also, is a rock slide of quartzite said to contain 1.5 million tons of ore of 0.3 per cent WO_3.

(b) Department of Cochabamba

1. The Kami Mine, in the province of Ayopaya on the east side of the river. This mine has been one of the most important tungsten producers in Bolivia. The quartz-wolframite veins occur in quartzites and metamorphic schists and the veins mined ranged from 4 inches to 4 feet in width and contain from 1 to 4 per cent WO_3.

(c) Department of Oruro

1. The Juliana Mine, 30 miles north of Oruro on the Condeauque Range. The deposit consists of a brecciated quartzite mass several meters wide

and 560 feet long. The matrix of this ore body is made up of scheelite and ankerite with barite, quartz and pyrite. The average tenor of the ore is 2 per cent WO_3, but in places ore containing from 5 to 9 per cent WO_3 is mined.

2. The Ascensión Mine, 18 miles northeast of Oruro in the Condeauque Range. The deposits consist of a large series of parallel veins and stringers, all with a general north-south strike. In general the width of the veins varies from 32 to 40 inches. The wider veins carry scheelite and the narrower ones wolframite. The country rock consists of steeply dipping sandstone beds with a wide stratum of soft, impervious and decomposed shale, which parallels the main vein and often forms one of the walls. Regarding the formation of these veins, Hess writes: "Apparently the vein was originally composed of barite, a little quartz, and more or less siderite or iron-bearing calcite that is now represented by friable iron-stained material. No pyrite has so far been found in the mine, but were it the original iron-bearing mineral some would now be found even in the oxidized parts of the vein. After the vein had been formed it was crushed by faulting, and scheelite, probably accompanied by a little quartz, filled cracks and spaces in the barite, recementing the vein just as the Jorge Quinto lode was recemented by adularia. There was probably also a later deposition of a little barite and quartz. As in the Jorge Quinto vein also, movement again took place after the recementation, so that the vein was crushed a second time, and as it is very crooked, the crushing is both fine and general over the extent of the vein." At present the average grade of ore mined is about 3 per cent WO_3.

3. The Senor de Quillacas Mine, 2 miles east of the Juliana Mine. Here are a number of narrow veins of ferberite up to a foot in width, which average 2.5 per cent WO_3.

(d) Department of Potosi

1. The Tasna mine, in the province of Nor Chichas. The tungsten vein is only 4 to 6 inches in width, high in grade, and traverses the metamorphosed slates and quartzites.

2. The Chorolque mine, in the province of Sur Chichas. Here complex tungsten and tin veins occur in a rhyolite intrusive mass 5,000 feet in diameter.

The tungsten deposits of the various mines described above may be grouped according to their temperature of formation thus:

1. Hypothermal deposits at Hucumarini, Mercedes del Illampu, Chojlla, Santa Ana, Enramada, Liliana, Aceromarca, Bolsa Negra, Cerro Negro, Araca, Pacuni, Pajchiri, Kami, Tasna.

2. Mesothermal and Epithermal deposits at Juliana, Ascensión.

1. Province of San Luis[36]

1. Los Condores mine is considered to be the largest tungsten mine in Argentina. It is situated about 10 kilometers from the town of Concaran, Province of San Luis. At this mine the country rock consists of a gneiss or phyllite schist with a general N 15° E strike and a relatively flat dip. Cross-cutting these beds at right angles are the ore veins striking N 75° W, with vertical dips. These main vein deposits are of massive quartz containing some tourmaline with wolfram and scheelite and small quantities of bismuthinite, pyrite and chalcopyrite. Narrow veins interbedded in the schists intersect the main veins and at the junctions enrichments are said to occur. Fault planes are encountered in the mine but these cause only minor displacements.

The tungsten minerals are both scattered and in clusters, and occasionally in rich pockets irregularly distributed both horizontally and vertically in the veins. There are two main veins about sixty feet apart, the South vein averaging 6 feet in width and developed over a length of 2,500 feet, and the North vein, which is narrower, but richer, and is developed over a length of 1,600 feet. Besides these there are two smaller veins, No. 2B and No. 3, which have been discovered in recent years and are now being explored.

2. Los Avestruces Mine lies 60 miles west of the railway station of Concaran in the Department of San Martin. Three main veins have been exploited; these occur in the metamorphic schists at or near the granitic intrusive mass. They have nearly vertical dips and vary from two to six feet in width. Locally lenses of rich ore occur along the veins and much biotite, containing some scheelite, is present. The ore is said to contain from 1 to 2 per cent WO_3, the percentage of scheelite being greater than that of wolframite.

3. El Morro No. 1 Mine lies 13 miles southeast of La Toma. Here irregular veins one to six feet wide occur in the schistose beds with some limestone, and have been traced over a length of about two miles. The ore is scheelite with tourmaline, chlorite and some fluorite, and is said to contain 1 to 1.5 per cent scheelite.

4. Los Reventones Mine is 30 miles west of Concaran. Here the deposit consists of a fracture zone in the schistose rocks with veinlets of scheelite accompanied by actinolite, garnet, epidote quartz, calcite, pyrite and zincblende.

5. La Aspereza Mine is situated at Tilisarao in the Department of Chacaubuco. The deposit here is also in a fracture zone in the mica schists which are intruded by pegmatite dikes, the ore occurring in irregular mineralized masses up to 60 feet long, 15 feet wide and developed for 25 feet in depth with scheelite, actinolite, biotite and epidote.

2. Province of Cordoba

1. San Virgilo Mine is reached by an autoroad from Los Condorese to Carpinteria, a distance of 40 miles and then about 20 miles by mule. Here the ore is found in a fracture zone in the schists a few hundred feet wide and several hundred feet long in concentrations on the side of the zone and in veinlets throughout the zone.
2. La Bismutina Mine is reached by an autoroad from Concaran which passes through the towns of Villa Dolores, Nueva C. and Salsacata, the distance to the mine being about 300 kilometers. The ore at this mine occurs in a series of interbedded quartz veins in schists, five of which have been developed. The veins are from one to two feet wide and occur at vertical intervals of 60 to 160 feet. The wolframite occurs in pockets, usually along the vein walls.
3. San Ignasio Mine is in the District of San Alberto. Four main veins have been developed, but with only slight production.
4. Auti Mine is situated 40 miles northwest of the Bismutina Mine. Three parallel fissure veins with a general east-west strike and a dip of 70° to the south have been developed over a few miles in length, the average width being about 2 feet. Both wolframite and scheelite occur with much mica, tourmaline and pyrite.

3. Province of Catamarca

The principal producing tungsten mine in this province is San Antonio in the Sierra La Ramada, 14 miles southwest of the town of Londres. The areas consist of schists intruded by granite which in turn are intruded by dikes of aplite and quartz veins. There are many of these veins striking in various directions from a few inches to a few feet wide in which the wolframite occurs in pockets with tourmaline, pyrite, beryl, and mica.

4. Province of San Juan

There is a group of several tungsten mines in this province, the San Rafael and Guardia Vieja being the most important. These are 30 miles southwest of the town Rodeo. Here "mantos" or horizontal deposits in the quartzites and shales, from 1 to 3 feet wide and some tens of feet apart, occur within a vertical distance of 200 feet.

5. Province of Mendoza

The Josefina is the only producer in this province, being 28 miles west of Tunuyan, Department of Tupungato. Here three parallel veins have been worked; these are from one to three feet wide and were developed at three levels over a length of about 1,000 feet and a depth of 200 feet. In these the wolframite occurs in isolated crystals and pockets in the quartz together with zincblende, molybdenite, and fluorite.

PERU AND CHILE

Most of the Peruvian deposits are situated near the valley of the Chuquicari, on the Pelagatos and Tamboras Mountains, in the departments of Ancachs and Libertad. In general, the Tungsten belt is about 45 miles long and a little over 4 miles wide. The principal mines are grouped about four centers: Ogopito, Lacabamba, Pasto Bueno and Jamboras. The veins which are typical epithermal veins vary in width from a few inches to over two feet and can sometimes be followed on the surface for a distance of several miles. Besides quartz, which is the principal mineral, the most abundant sulfide mineral is pyrite, followed by wolframite, sphalerite, tetrahedrite, enargite and galena.[57]

In Mt. Huaura are found two large quartz veins, between 5 and 25 meters thick, cutting through sandstones and slates, which have been invaded by granite. The vein minerals are hübnerite, pyrite, gray copper and galena, in a gangue of quartz and fluorspar.

Tungsten ores were reported to have been discovered in the departments Tayabama and Huancavelica.

It is said that the Julcani mine, an old lead-silver property in the central part of Peru, has as reserves 2½ million tons of low-grade tungsten ore.

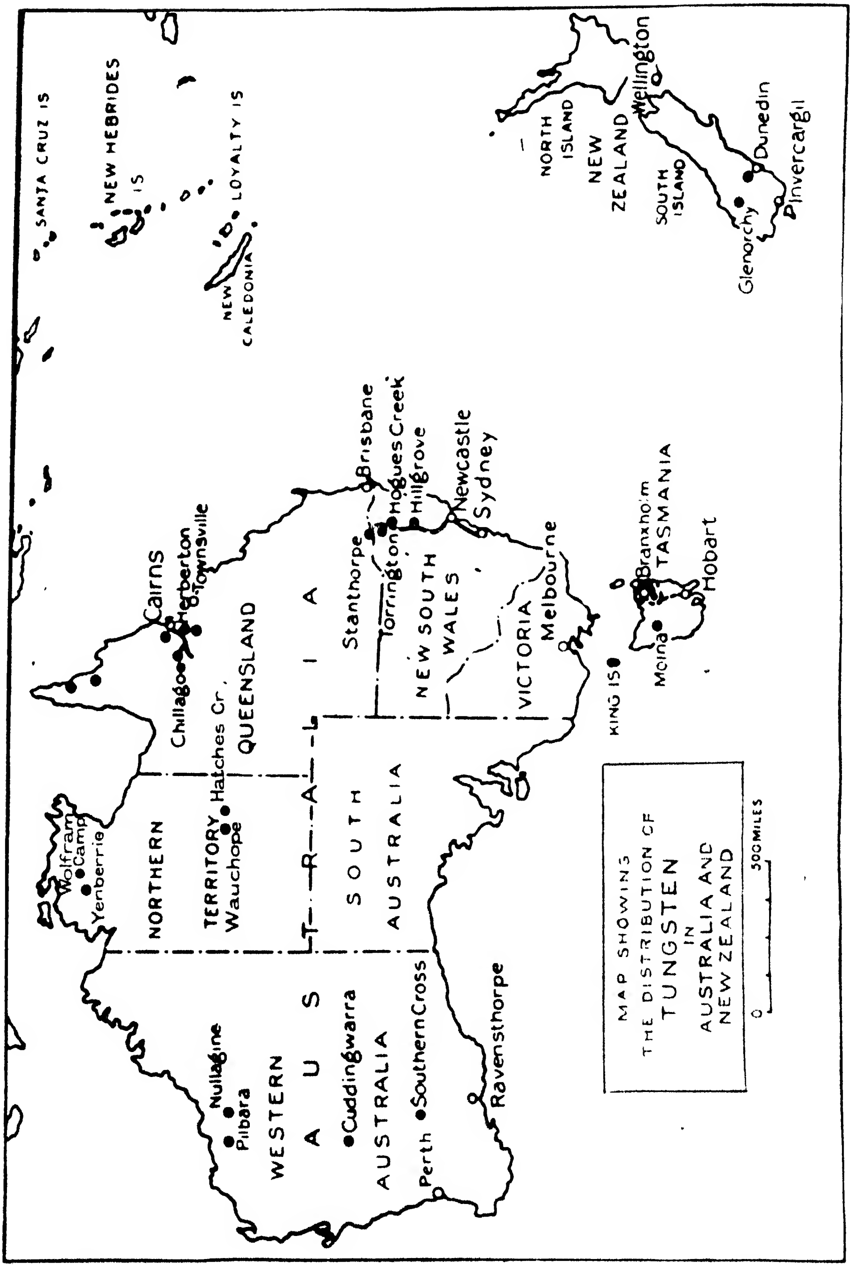
In Chile the tungsten deposits are located in the province of Tacna, not very far from the port of Arica, on the River Lluta. Production has been insignificant.

AUSTRALIA

Excepting Northern Territory, Western Australia and New Zealand, tungsten deposits of commercial value are scattered along the eastern coastal cordilleras, from Queensland, through New South Wales and Victoria to Tasmania. In this zone, near the contact of granite and sediments, are found also deposits of many metals, notably copper, gold, and tin. The metals which most commonly accompany tungsten are bismuth and molybdenum, which sometimes occur in sufficient quantity to repay extraction; on the contrary, scheelite, where it occurs, is generally associated with siliceous gold ores and sometimes with antimony.

(a) Queensland

The principal producing localities are Mt. Carbine in the Herberton mineral field and Wolfram and Bamford in the Chillagoe mineral field. The deposits occur both in the granite and the sediments close to the



Distribution of tungsten in Australia and New Zealand.

contacts, in pegmatites and quartz veins. The ore consists principally of wolfram, with only a little scheelite and bismuth and molybdenum.

Mt. Carbine. Here the pegmatite lodes are tabular in form and are arranged in about twelve radiating zones. The gangue minerals are quartz and feldspar; where feldspar is in greater amount, the wolfram becomes richer. The width of the veins varies from a few inches up to 6 feet, the average being 2 feet.

Wolfram Camp. Wolfram mineral with bismuth and molybdenite is found in contraction fissures in the granite and in a series of irregular pipes in the greisen. The horizontal fissures are never more than 10 to 12 inches wide, while the vertical veins sometimes increase for a short distance to a width of from 3 to 4 feet.

Bamford. The ore deposits found here are similar in character to those found at Wolfram Camp. Here scheelite is quite common as a secondary mineral after wolfram.

(b) New South Wales

The principal deposits are in a quartz-topaz rock which contain some bismuth, fluorspar, beryl, monazite, chlorite and hornblende. The deposits are apparently replaced tongues of granitic rocks which invaded sandstones and other siliceous sediments. Other deposits in the northeastern and southeastern parts of the state are pipes in a granitic rock.

The Hillgrove Scheelite Deposits.[37] "These are found in lenticular patches along the contact of gneissic granite and a spotted slate, and also as well-defined lodes associated with siliceous gold-reefs in the granite and slates. The scheelite veins are generally found on either side of the gold-reefs and parallel to them, though in some of them gold ore gives place to scheelite in patches. They are from 1½ to 6 inches wide, and are richest where they are cut by cross courses or faulted, some of them occupying the fissure veins, while others fill contraction cracks in the granite. The ore is patchy and the values tend to increase downwards, as do those of the gold ores. The values have been proved to persist to a depth of over 1,500 feet in the deposits on the sides of Baker's Creek Gorge, and have been followed to 200 feet in the Baker's Creek and Proprietary Mines. The gangue is chiefly quartz, and the scheelite is often associated with stibnite. The mineralized area is 4 miles long by 2 miles broad, and contains several mines, including the Bullfrog, Hopetown and Damifino Mines, the last being by far the largest producer."

The Mole Tableland, near Torrington, is the most important wolfram mining district. The deposits occur as fissure veins and pegmatites in the slates and as lodes along the center of greisenized zones in the granite.

The ore carries principally wolfram with bismuthinite in subsidiary quantities.

About 20 miles from Broken Hill there occur several parallel wolfram-bearing lodes in micaceous schist, and quartzite which have been proved over a distance of between 9 and 11 miles. The wolfram content of the ore varies from 2 to 6 per cent WO_3.

(c) Victoria

The output from this state has always been small. Mention may be made of the occurrences at Mt. Murphy near Benambra, Lintons near Baragwanatti, and at Maldon on the Buckwong River.

(d) Tasmania

In recent years Tasmania has topped the other States in production. Storey's Creek and Moina are the two principal producing localities. The deposits, in the form of quartz veins, greisenized bands and pegmatites and irregular pipes like those of Bamford in Queensland, occur in either quartzites and slates or quartzites and limestones, invaded by granites of the Devonian age.

At Storey's Creek, near Avoca on Ben Lomond, wolframite occurs in two quartz veins, 2 to 6 feet wide, cutting quartzite. The associated minerals are cassiterite, bismuthinite, topaz, beryl and fluorite.

In the Middlesex district in northwestern Tasmania, numerous deposits carry wolframite, cassiterite and bismuth. The best deposit is that of the Sheppard and Murphy Mine at Moina. Seven or more veins, three of which are of more or less economic importance, cut quartzite and tactite near a mass of intrusive granite and granite porphyry. They reach a length of 1,400 feet and are from 6 to 30 inches thick but are usually only from 6 to 12 inches thick. They have been worked for a length of 1,000 feet.

One of the most important tin and wolfram producing mines in Tasmania is the Aberfoyle mine, situated at Rossarden 40 miles southeast of Launceston. The tin and wolfram deposits are chiefly quartz and greisen veins, occurring in both the granite and intruded slates. The ore consists of quartz with veinlets or scattered grains of cassiterite, wolfram, pyrite and a little zincblende and fluorite.

Besides cassiterite and wolframite the Sheppard and Murphy lodes carry some scheelite, bismuthinite, bismuth, bismutite, pyrite, pyrrhotite, a little molybdenite, chalcopyrite and galena, with quartz, fluorspar, topaz, pinite, gilbertite, laumontite and beryl. The lodes are said to have "a pegmatitic structure." They carry more ore where they cut the tactite than they do in the quartzite.

The All Nations wolframite mine, a short distance east of the Sheppard and Murphy Mine, has a less complicated mineral assemblage, but carries some gold.

The Dolcoath, Squib, Premier and Hidden Treasure are among other and smaller mines of the district. The geology differs considerably from mine to mine.

The King Island scheelite deposit on King Island, off the northwest corner of Tasmania, is the largest tungsten producer in the Commonwealth and may be considered as one of the largest scheelite deposits in the world. It has been proved by extensive drilling that there are about 1,100,000 tons of 0.8 per cent WO_3 payable ore in the deposit. The ore bodies occur in a series of slates which in turn are intruded by aplites and granite magma. The main associated minerals are garnet and quartz.

(e) **New Zealand**

Tungsten deposits occur in several places in New Zealand, principally at Macrae's Flat, 50 miles north of Dunedin, in Marlborough province, Central Otago; and in the Glenorchy area at the head of Lake Wakatipu. The last-named area is the most important and best known of the producing localities.

The country rock is quartzose, mica schist, graduating into phyllite and slate. "The veins are of two types, fissure veins at Glenorchy and elsewhere, and bedded or segregated veins at Macrae's Flat. They are also divided into two types economically, those which are worked mainly for their scheelite content, with gold as a by-product, and are treated by coarse crushing, as at the Glenorchy mine and Golden Point, and those worked chiefly for their gold content, with scheelite as a by-product, as at the Highlay Mine, Macrae's Flat.[38]

In the Macrae's Flat district, the mineralized belt is from ½ to 2 miles wide and extends for a distance of 16 miles. At the Golden Point Mine there are three lodes, the middle of which is from 3 to 6 feet wide and carries ½ to 1 oz of cold to the ton. Besides scheelite and gold, the ore carries quartz, pyrites, arsenic, sulfur and rhodonite.

In the Glenorchy area the lode is from 1 to 8 feet wide and extends for nearly a mile along the strike. The gangue is dense quartz with gold, scheelite, pyrite and mispickel.

(f) **Northern Territory and Western Australia**

During recent years the output of tungsten ore from Northern Territory comes next to that from Tasmania; the output from Western Australia may be considered negligible.

In the northern end of Northern Territory are two small tungsten fields, Wolfram Camp and Yenberrie, which were discovered early in this century. They are on the edge of a mass of granite known as the Pine Creek massif. Wolfram Camp is in E. long. 132° 16′ and S. lat. 14°. Yenberrie is possibly 20 miles southwest of Wolfram Camp.

At Wolfram Camp, "Burn's Wolfram Mine", the deposits are in lenticular quartz veins or masses, most of which carry wolframite with chalcopyrite, and are enclosed in mica-quartz schist and hornfels. In some places the chalcopyrite is much in excess of the wolframite. There is some molybdenite, a little bismuth, and tin in neighboring deposits. Some alluvial wolframite has been mined and a little scheelite has been found in veins.

In the Yenberrie field, wolframite and molybdenite are found in quartz veins cutting greisen (quartz and white mica with spots of albite) and in less quantity in the greisen itself. Nine such deposits have been mapped. The largest deposit is about 1,000 feet long and the greisen reaches a width of 60 or 70 feet, but the quartz vein in the middle is only about a foot thick. Only the quartz is worked.

Wolframite is in excess in most veins, but in one molybdenite is in the greater quantity. Arsenopyrite, copper minerals, pyrite and a little bismuth are also found with the wolframite. The deposits are apparently of less importance than those at Wolfram Camp.

What seem to be large deposits are found at Hatches Creek at about E. long. 135° 10′, 2. lat. 20° 47′; and at Wauchope, 60 miles west of Hatches Creek and 16 miles southeast from Wycliffe well on the Adelaide-Port Darwin telegraph line and trail. Both groups of deposits are in the Davison Range.

At Hatches Creek the tungsten-bearing area is 5 miles long from north to south and a mile wide. Sandstones, conglomerate, slate and schistose granite form the country rocks. One of the quartzites "the blue metamorphic quartzite", has been intruded by diorite. Wolframite-bearing quartz veins cut the diorite and split and die out in the overlying quartzite. The veins are from an inch to 4½ feet wide and are as much as ¼ mile long, but are very irregular. Wolframite is the tungsten mineral in most of the field, and with it the veins carry iron and bismuth oxides, copper carbonates, some muscovite and a very little molybdenite. The quartz breaks with very sharp edges. At the north end of the field scheelite is the dominant tungsten mineral.

The Wauchope field covers a small area of about ¼ mile by ⅗ mile. A series of quartz veins 1 inch to 2 feet wide are as much as 800 feet long, and are remarkably uniform. They are bedded in "metamorphic sandstone and slate" and are comparatively flat.

In Western Australia, wolfram and scheelite are found associated with gold ores in a number of localities, but their output has been insignificant. Mention may be made of the occurrences at Nullagine, Pibara, Cuddingwarra and Southern Cross.

JAPAN AND CHOSEN

It is reported that there are six tungsten-producing mines in Japan, one in Gifu prefecture and five in Hamaguchi prefecture. In the former, scheelite associated with galena and zincblende occurs near the contact of quartz-porphyry dike with crystalline limestone; in the latter, scheelite is sometimes associated with chalcopyrite, pyrrhotite and zincblende, the gangue minerals being hedenbergite, garnet and a little quartz and fluorite.

In Chosen, important deposits of tungsten are found in the central and south central parts of the peninsula, in the provinces of Kogen, North Chusei, North Keisho and South Heian. The deposits in the first two provinces have produced more than three-fourths of the total output of Chosen. All deposits thus far developed occur as distinct veins and contact deposits, or as placer deposits from these. Associated with the wolframite are pyrite, chalcopyrite, arsenopyrite, cassiterite, molybdenite, quartz, calcite, fluorite, and less commonly, scheelite, sphalerite and galena. With the scheelite occur arsenopyrite, pyrite, chalcopyrite, cuprotungstite, molybdenite, quartz, fluorite and calcite.

THE IBERIAN PENINSULA

Tungsten ores in Spain and Portugal occur as both vein and placer deposits at or near the contact of Cambrian schist and younger granite in a formation which runs roughly northwest-southeast over the western half of the Iberian Peninsula. By far the predominating mineral is wolframite, but considerable scheelite is found in the Salamanca and Orense provinces of Spain as well as the Guarda area of Portugal. The tungsten ore is most often accompanied by cassiterite and to a lesser degree by the iron minerals ilmenite and pyrite. In most of the vein deposits small amounts of arsenopyrite and chalcopyrite are found with the wolframite, and in the southern-most zones considerable bismuth accompanies the tungsten mineral. There are also indications that columbo-tantalite occur in a few of the northern ores, especially when the wolframite is found with alluvial tin.

Broadly speaking, there are only four mines on the Iberian Peninsula which can be considered as being capable of continuing operation under normal market conditions. These are, in order of their importance: Panasquiera and Borralha in Portugal, Silleda and San Finx in Spain. Together these four mines account for about 50 per cent of the total tungsten output of the Peninsula.

An additional 30 per cent of the Iberian Peninsula's tungsten is supplied today by some 40 to 50 smaller mines whose individual output may vary anywhere from 1 to 10 tons per month. Some of these deposits have small but reasonably efficient concentrating plants, while others have nothing more than primitive hand-washing operations; but practically none of these "secondary" mines have proved ore reserves for a successful commercial operation once the present war is over. Producers such as Alianza, Sabrosa, Matas da Rainha and Riberia in Portugal, and Casayo, Reconquista, Maria de los Angeles, and Tres Amigos in Spain, are just a few examples of mines which fall into this class. The balance of Spain and Portugal's tungsten production comes today from the countless "scratchings and pickings" which are found scattered over the entire mineralized area.

We may say that Spain and Portugal's combined normal tungsten production of about 250 tons a month of concentrate has today been more than doubled as a result of the almost insatiable German demand for wolfram. This increase has come principally from marginal deposits and "fossicking" operations made possible by the abnormal prices being paid for tungsten on the Peninsula.

(1) Portugal

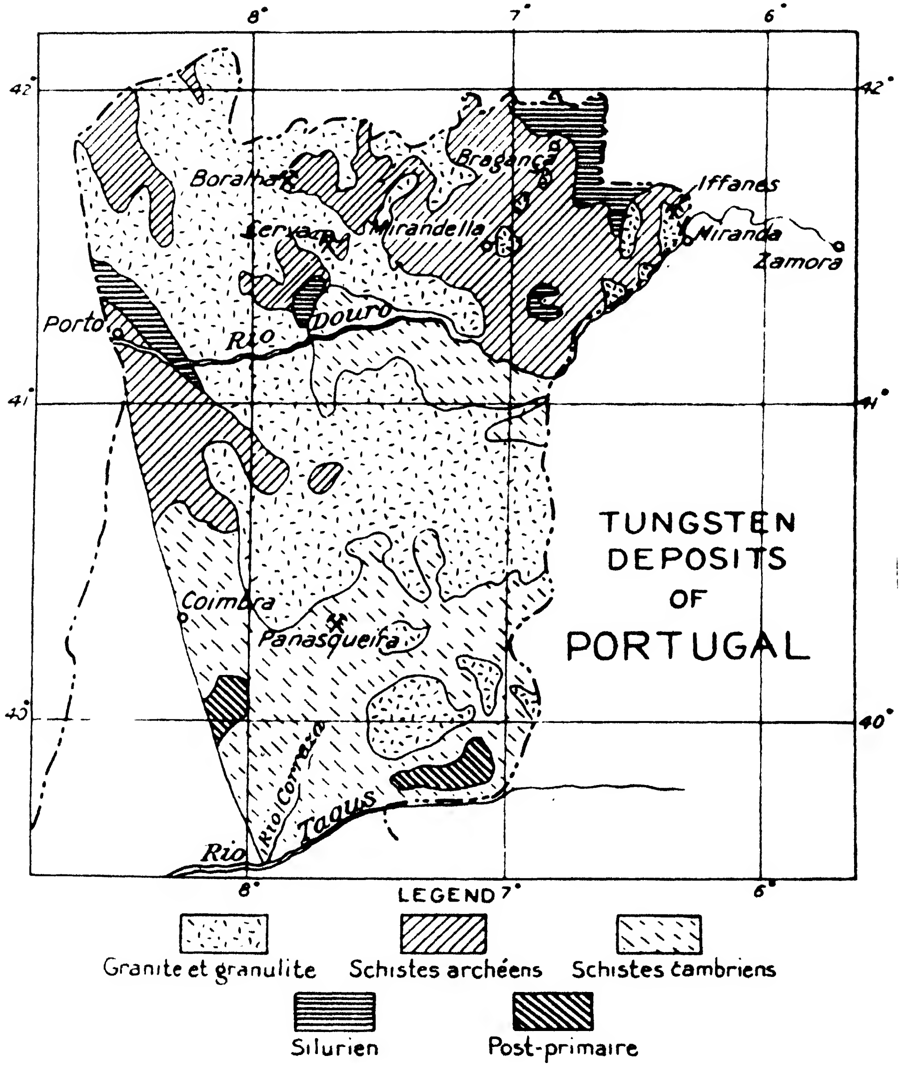
In Portugal are found the most extensive tungsten deposits of Europe. Most of the Portuguese tungsten deposits are in Trasos-Montes, in the northeast part of the country. Practically all are north of the Tagus River.

Wolframite is the ordinary tungsten mineral. Ferberite, hübnerite, and scheelite are also found. The wolframite occurs in quartz veins cutting granite and the gneiss, hornfels and schist into which it is intruded. Cassiterite accompanies the wolframite in most veins though veins near Iffanaes and Cerva, in the northeast and north central part apparently contain none. Other minerals accompanying the wolframite are pyrite, chalcopyrite, zincblende, galena and arsenopyrite and their oxidized forms. Some veins also carry muscovite, tourmaline and fluorite. The veins are said to be from 1 to 60 inches wide and to average 12 inches, and reach a length of about a mile. They seem to average 1 to 1¼ per cent WO_3, and it is said that very few have been worked below water level.

Arsenopyrite accompanying wolframite in the Fraga de Venda veins is reported to carry 250 grams of silver and 4 grams of gold per metric ton (7.1 oz Ag and 0.13 oz Au per short ton), and zincblende to carry 210 grams of silver and 10 grams of gold (6.7 oz Ag and 0.32 oz Au per short ton).

The Panasqueira Wolfram Mine is the largest tungsten mine in Portugal. It is operated by the Beralt Tin and Wolfram Co., a British Corporation.

It is situated near the town of Silvares in the Serra da Estrella, highest mountain range in Portugal. A series of rich parallel seams of wolfram have been attacked through long adits and the ore carried by cableway



Tungsten deposits of Portugal.

down to a much re-vamped mill on the upper reaches of the Zezere river. Under the stimulus of war production, Panasquiera's output has steadily risen from about 100 tons a month early in 1942 to over 200 tons monthly by the end of the year. This, for the moment, is a probable peak in production, for any increase beyond that is hampered by the size of the cableway and the capacity of the now rather over burdened concentrating plant. The product is a high-grade (70 per cent plus) WO_3 concentrate with very low tin and arsenic content, and has during the past few years formed Britain's principal source of tungsten.

Borralha: The mine is located in the Serra das Alturas in the northern part of Portugal, just south of the highway from Braga to Chaves and about equally distant from those two towns. It is owned and operated by a French company who sell their output to the British under an existing old contract. Steep dikes containing wolframite and pyrite in quartz are mined at various levels and the ore treated by jigs, tables and separators at a not-too-modern plant. Production has been maintained at an average of 40 tons a month of high grade concentrates during most of 1942.

(2) **Spain**

Silleda: This is Spain's largest wolfram producer, situated in the province of Pontevedra in the northwestern part of Spain (Galicia). The mine was lost several years ago to its original French owners and is now operated by a Spanish group. The parallel, almost vertical veins contain considerable cassiterite in addition to wolframite, and the mine normally produces about one-half ton of tin for every ton of tungsten ore. Lack of proper mining and milling equipment has been the serious bottleneck to Silleda's output, but recent improvement in the concentrating plant practically assures a continuance of their present production of about 25 tons a month of wolfram concentrate.

San Finx: Originally and still fundamentally a tin deposit, this mine was in British hands until several years ago, when it was sold to the Spanish "Industrias Gallegas." It is located just a few miles from the Atlantic coast near the town of Noya in the province of La Coruna (Galicia). Lack of efficient technical direction plus failure to obtain essential machinery has seriously impaired production and today, in spite of the war impetus, many sections of the rather wide well-mineralized lode are practically abandoned. Present output is in the neighborhood of 10 tons a month of wolfram concentrates with about twice that quantity of cassiterite.

CORNWALL

The production of tungsten ore in Cornwall has been quite irregular and is comparatively small.

The wolfram-producing lodes are nearly always situated near the contact of the granite and the so-called killas. Killas is the country rock, composed of altered slaty sediments. It is observed that in Cornwall wolfram is most abundant in the upper part of the tin zone and is below the rich copper zone.

The most important wolfram-producing mines in Cornwall are located in Camborne and Redruth. The ore mined here is very complex, containing tin, copper, tungsten and arsenic with smaller amounts of silver, lead, zinc, bismuth, cobalt, nickel, molybdenum, manganese, iron and uranium.

Other producing localities are St. Austell, Bodmin, Moore, Callington and Tavistock.

BRAZIL[49, 50]

With the discovery of scheelite deposits in the States of Paraiba and Rio Grande do Norte, Northeastern Brazil, in early 1942, Brazil is now looming up as a great future producer of tungsten ore. In previous years wolframite was known to occur in the States of São Paulo, Santa Catharina and Rio Grande do Sul, Southeastern Brazil, but its production has been small.

At least 60 scheelite localities have so far been discovered in Northeastern Brazil, distributed throughout an area of about 15,000 sq. km. Similar geological structure, favorable to deposition of scheelite, has been observed to cover more than 100,000 sq. km in these two states. However, the tenor of the ore is comparatively low and hence future production of the ore will be conditioned by the movement of market price paid for it. The 1944 production was about 1,500 metric tons.

1. Paraiba and Rio Grande do Norte

Geology: "With the exception of a narrow coastal belt of Crestaceous and later sediment, the rocks of Northeastern Brazil belong to the crystalline complex of the Brazilian shield. Mica schists, called the Serido series by L. J. de Moracs, with interbedded limestones, marbles, and quartzites have been intruded by great granite batholiths, following by pegmatites which yield important quantities of cassiterite, tantalite, beryl, and quartz veins. The mica schists were tightly folded; pure limestones were converted into marble and impure limestones into amphibolite. Many phenomena of contact metamorphism were developed in the older rocks including limestones altered to scheelite—bearing tactites".

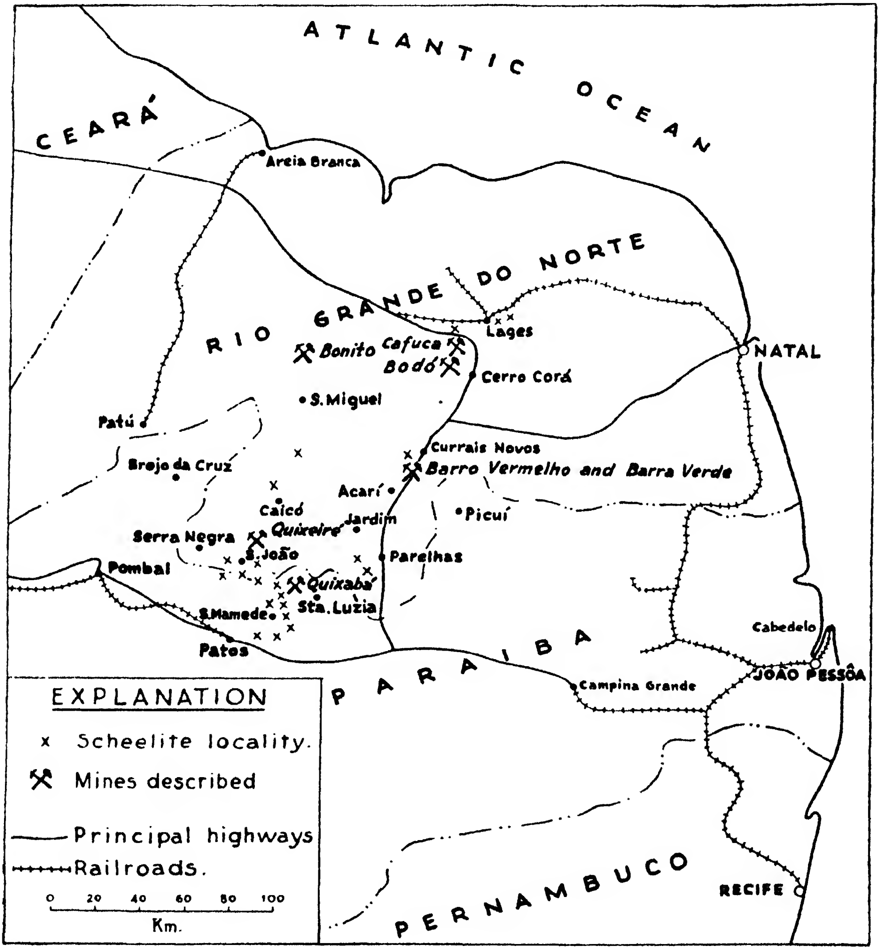
Ore Deposits: "With one possible exception, the scheelite ore bodies all lie in or very near to calcareous beds intercalated in the mica schists of the Serido series. All are marked by the presence of epidote, garnet, or quartz. One or more of these minerals may serve as guides to ore.

"The calcareous beds range from pure crystalline marbles to amphibolites. In general, where a pure marble and clayey marble or an amphibolite occur close together, it is the impure marble or the amphibolite that is mineralized.

"In wider calcareous beds the strongest mineralization generally is in the marble or amphibolite in contact with the enclosing mica schist;

indeed a schist contact appears to be a necessary requisite for the mineralization in the wider and purer marble beds.

"Quartz veins also carry scheelite, but generally only when they cut calcareous rocks."



Map showing location of scheelite deposits in Brazil. *After W. D. Johnston, Jr., and Francisco Moacyr.*

Mineralogy: "The principal contact metamorphic minerals developed in the limestones of the region are epidote, garnet, and quartz; vesuvianite, wollastonite, hornblende, scapolite, and scheelite are widely spread but less abundant. Molybdenite has been found in several mines and a few tons of bismutite have been recovered from scheelite placers.

"Andradite garnet forms district as well as irregular aggregates of crystals in the calcareous beds. Although garnet and epidote usually occur together at some mines, such as the Caieira, epidote is rare and garnet is the dominant ore guide. Elsewhere, as at the Bonito mine, garnet is rare, and is formed only in small crystals in the panned scheelite concentrates.

"Epidote is present in all of the scheelite deposits. In the calcareous rocks that have not been strongly silicified it occurs in small crystals of fine grained masses whereas in highly silicified beds it forms large flat plates.

"Quartz is also an ore guide, ranking in importance with garnet and epidote. It may replace limestone, or have the form of lit-par-lit lenses in schist as at the Riacho Felchado mine. Quartz veins are to be seen at most of the mines and prospects, and may of these veins carry scheelite. 'Scapolite occurs in short stubby prisms, wollastonite and hornblende in fibrous aggregates, and vesuvianite in characteristic tegragonal prisms.

"Scheelite generally occurs in crystals, less than 1 cm in diameter and the average size is near 1 to 2 mm. At some mines, however, crystals weighing 500 grams to 1 kilogram are not uncommon; the largest at Vermelho mine weigh 2.2 kilos.

"Generally the scheelite of the region is white to light grey in color, but it may be dark grey to dark green.

"Several tons of bismutite have been recovered from residual placers of scheelite, notably at the Bonito, and Barro Vermelho mines. It is uncertain whether bismuth minerals were formed during the tactization of the limestones or belong to a later pulse of mineralization. A specimen from the Barro Vermelho mine which consisted of milky quartz containing a veinlet of metallic bismuth altered on its edges to bismutite, strongly suggested that the coincidence of bismuth minerals with scheelite was a matter of superimposed mineralization rather than contemporaneousness.

"Chalcedony replaces limestone in some mines, notably at the Bodo. Apatite, in small (1–2 mm) blue prisms, was seen only at the Jetai Mine."

Origin: "The broad picture of the scheelite region is one of roof pendants of schist within a field of batholitic granites. This geologic environment of meta-sedimentary rocks intruded by granites and cut by their accompanying pegmatites and quartz veins has provided the opportunity for many contact metamorphic phenomena.

"Granites at their centers of intrusion are characteristic and distinctive, but outward from these centers they merge with the schist through peripheral zones of granitized schists with the aspect of a granite gneiss. Such granitization of the schists is marked by the introduction of potash feldspar into the schist, commonly in large phenocrysts, by a coarsening of the grain size of biotite, hornblende and quartz originally present in the schist, and by the introduction of many thin lit-par-lit pegmatites. Such granitization appears to represent the first and most intense alteration of the schist.

"Tungsten-bearing solutions originating in the granites appear to have moved through the schist beyond the outer limit of granitization and to have been deposited when they came in contact with calcareous beds.

"The localization of the scheelite-bearing tactite in the impure limestone in preference to the crystalline marbles, indicates some kind of chemical control for which we do not, as yet, have sufficient data. The preferential location along schist contacts within calcareous beds appears to indicate that the schist or the contact itself, offered freer passage to mineralizing solutions than did the calcareous beds.

"Pegmatites, consisting of muscovite (and sometimes biotite), feldspar and quartz are present in most mines, but in a region characterized by its pegmatites, this is not necessarily of direct genetic significance. Indeed, it would be difficult to find a square kilometer in the scheelite region what did not have outcrops of pegmatite. Perhaps the most significant observation on the role of pegmatites in tungsten mineralization is the fact that the pegmatites at the Pitombas mine are fractured, and epidote, usually the handmaiden of scheelite, heals the fractures.

"Quartz veins sometimes carry scheelite and probably are more directly related to tungsten mineralization than are either the granites themselves or the pegmatites.

"It seems reasonable to conclude that these deposits can be broadly classified as being of contact metamorphic origin wherein the tungsten-bearing solutions, coming late in the metamorphic process, deposited scheelite in some of the calcareous rocks."

Size and Grade of Ore-Bodies: "In several of the larger mines, ore *zones* have been traced along the strike of calcareous beds for a distance of 1 km or more. In these larger mines a pattern of ore shoots appears to be developing. Certainly, experience to date indicates that the one bed varies greatly in its scheelite content as it is traced along the strike.

"The only quantitative data at hand is Dr. Sandoval Carneiro de Almeida's exploration of the Bonito mine. He found that in 20 trenches across the ore zone about 10 per cent of the lineal distance was through material yielding more than 1.8 kilos of scheelite per ton, 15 per cent was through material yielding 1.1 to 1.8 kilos per ton, and the remainder yielding less than 1.1 kilos per ton.

"From ultraviolet lamp examinations of the hard ore of the larger mines, we formed the impression that most of the primary ore in the region contained less than 0.5 per cent WO_3, although some small pockets containing, perhaps, up to 1.5 per cent WO_3 were seen. In some mines, however, there is a surface blanket enriched by residual concentration of scheelite.

"The grade of the concentrates ranges from 70 to 75 per cent WO_3, depending upon how well the material has been washed. In the final hand panning, losses are high."

The following table gives a summary of the principal mines in the States of Paraiba and Rio Grande de Norte.

Mine	Location (Municipality)	Characteristics	Grade of Ore
Brejui	Currais Novos	Scheelite is found in the tactite layer, 0.5 to 1.5 m thick, between the schist and granite.	Average content of scheelite along the surface is about 1.5%. At present this mine is the largest tungsten producer. The 1944 production was 406 metric tons constituting, as it did, about 28% of the total Brazilian scheelite production.
Quixaba	Sta. Luzia	Scheelite occurs along contacts of thin impure marble beds and schist with epidote, garnet and scapolite; mineralized zone extends for a distance of 1½ km; no scheelite is found in the quartz veins.	Ore averages 0.1% WO_3, but selective mining might yield ore of 0.5% WO_3 or better; output per man-day was 2.5 kg, highest in the region.
Quixere	Serra Negra	Scheelite most abundant in marble relics that have not been altered to amphibolite; the latter conforming with walls of granitized schist, is 1½ to 2 m. wide. Where amphibolite has been epidotized scheelite appears most abundant at schist contact.	Av. scheelite content appears less than 0.5%.
Bonito	S. Miguel da Jucurutu	The epidotized amphibolite zone, interbedding with schists, is 2 to 10 m. wide and 1400 m. long and is cut by a network of quartz veins. Scheelite occurs in quartz veins and in adjacent walls of epidotized amphibolite. Associated minerals are bismutite, pyrite, molybdenite. Garnet is rare and is not as common as in other scheelite deposits in northeastern Brazil. Much of the scheelite recovered to date is in residual material.	Of the trenching so far done about 10% of the linear footage gave material yielding more than 1.8 kg of scheelite per ton and 15% gave material yielding between 1.1 and 1.8 kg per ton. Thus the bulk average is less than 0.1% WO_3. In the last week of July, 1943, the production was 8 tons and the man-day production was 0.62 kg scheelite.
Barra Verde and Barro Vermelho	Currais Novos	Interbedded in the Seriodo schist is a large lense of limestone, which can be traced for about 3½ km. In the Barro Vermelho mine, its width ranges from 150 to 300 m. and in the Barra Verde mine it is about 25 m. Mineralization consists of epidote, garnet, vesuvianite, some hornblende, and scheelite. The Barro Vermelho mine has produced more scheelite than any other mine in Brazil but is now closed on account of market condition. Most of the scheelite production has been from the residual mantle.	In July 1943 the production at the Barro Vermelho mine was near 130 tons and in the last week of July the man-day production was 1.0 kg scheelite. At the Barra Verde Mine, the distribution of scheelite appears to be very irregular, the ore averaging less than 0.5% scheelite.

Mine	Location (Municipality)	Characteristics	Grade of Ore
Bodo	Santana do Mato	Thin limestones interbedded in the Seriodo schist have been replaced by epidote, garnet, much quartz, and scheelite. Working has been confined to the weathered material. The beds which were replaced by quartz, however, have not been decomposed by weathering. It is planned to crush this hard material for the extraction of the contained scheelite by tabling.	The ore is said to contain about 1% scheelite This mine may now be considered the second largest producer. The 1944 production was 484 metric tons.
Cafuca	Santo do Mato	Thin limestone layers which range in thickness from a few centimeter to more than 5 meters, have been altered to an epidote and quartz tactite. Additional contact minerals in lesser amounts, are vesuvianite and wollastonite. Scheelite occurs with both epidote and quartz. These limestone layers are imbedded in Serido schist.	Much of the initial production came from residually enriched surface material
Sonto	Sta. Luzia	The mine consists of several open cuts exposing thin beds of limestone in mica schist. Some of the limestone beds contain garnet, epidote and scheelite.	In the last week of July, 1943 the production was 40 kg and the man-day production was 0.66 kg scheelite.
Rischo Caieira	Sta. Luzia	Several open cuts expose thin layers of clayey limestone interbedded in muscovite schist and quartzite. The limestones contain irregularly distributed patches of epidote and garnet that carry scheelite.	In the last week of July, 1943, the production was 120 kg and the man-day production was 0.8 kg scheelite.
Malhadino	Sta. Luzia	Several open cuts expose a thin steeply dipping limestone bed a few meters from the granite contact and parallel with it. Scheelite occurs in sparcely distributed patches of tactite and along narrow quartz veinlets that are concordant with mica schist.	In the last week of July, 1943, the production was 60 kg and the man-day production was 0.5 kg scheelite.
Sao Nicolao	Sta. Luzia	Two narrow vertical beds of limestone striking approximately parallel with the granite content and about 50 m. from it have been replaced in part by epidote, quartz and lesser amounts of garnet, scapolite and scheelite. Trenches and open cuts expose these beds for a striking distance of about 700 m. The limestone beds are less than 5 m. thick and have been worked to a maximum depth of 20 m.	The scheelite content of the limestone beds, as a whole, is less than 0.5%. The man-day production for the last week of July 1943, was 0.83 kg scheelite and during this week the production was 500 kg.

Mine	Location (Municipality)	Characteristics	Grade of Ore
Flamengo	Sta. Luzia	This prospect is characterized by a strong but short outcrop of layered quartz with garnet and epidote which carry scheelite.	
Pitombas	Patos	Scheelite occurs with sparcely distributed epidote in the limestone lenses and with epidotized amphibolite streaks within the muscovite schist.	The man-day production in last week of July, 1943 was 0.83 kg scheelite and the production in this week was 100 kg.
Jetai	Serra Negra	The mine consists of several open cuts, the deepest of which is 4 m., exposing muscovite schist, in which are found 1 to 5 beds of silicified and epidotized limestone containing sparcely distributed scheelite.	
Malhada dos Augicos	Jardim do Serido	A long series of open cuts expose steeply dipping narrow beds of limestone enclosed in muscovite schist. The limestone beds contain irregularly distributed clusters of epidote and garnet which carry scheelite. The principal limestone bed has been opened for a distance of about 1 km and a parallel bed for a distance of about 300 m. This is one of the best mines in the region.	The scheelite content of the limestone beds, as a whole, is probably less than 0.5%.
Caieira	Jardim do Serido	Marble and amphibolite, 1 to 2 m. thick, are interbedded with muscovite schist. Scheelite occurs with garnet while in the extreme western part of the mine where epidote is abundant, scheelite occurs with epidote. At the west end of the mine there are a number of quartz veins which carry a little scheelite.	In the last week of July, 1943, the production was 100 kg and the man-day production was 0.42 kg
Salgadinho	Caico	Scheelite associated with garnet and epidote, is found in a network of small quartz veinlets which cuts the schist. The zone of quartz veinlets is at least 20 m. wide.	The amount of scheelite does not exceed 0.2% of the material mined. In the last week of July, 1943, the production was 100 kg and the man-day production was 0.83 kg scheelite.
Riacho Fechado	Currais Novos	The outstanding characteristic of this mine is the occurrence of garnet, epidote and some scheelite in flat quartz lenses in mica schist.	

2. Sao Paulo

The Inhandjara mine is located 3 kilometers from the Itupeva railroad station. Its production in 1944 was 102.7 metric tons of wolframite. Wolframite occurs in quartz veins in the gneiss formation. There are over 20 veins but only five of them have been worked. The veins, some parallel, some crossing each other, are from 0.3 to over 1 meter in thickness and extend from a distance of 30 to several hundred meters. The average composition of the quartz veins is: Quartz—93 per cent, Topaz—3 per cent, Pyrite—1 per cent, wolframite—1 per cent, plus small amounts of cassiterite, sphalerite, molybdenite, chalcopyrite and pyrrhotite.

3. Santa Catharina

The wolframite prospect is located 16 kilometers from the town of Nova Trento. At present the wolframite production comes from the alluvial deposit which contains about 1 per cent wolframite.

4. Rio Grande do Sal

Wolframite has been found at Encruzilhada, where it occurs together with tin over an area of 20 square miles, in the ratio 1 : 10.

5. Salto do Pirafora (in the municipality of Sorocaba)

Wolframite has recently been found at a locality about 70 kilometers S-70-W of Itufeva. There are two sets of veins having an average thickness of 40 centimeters and a length of about 500 meters. The minerals found associated with the wolframite are bismuth and lead ochre, cassiterite and tourmaline.

AFRICA

Tungsten minerals, both scheelite and wolframite, are found mainly in Southern Rhodesia, Nigeria Union of South Africa and South-West Africa. Southern Rhodesia is the chief tungsten producer.

In Nigeria,[46] the wolframite deposits are found in the outcrops of younger (Archaean) granite, which have been intruded into a complex of older (Archaean) granite and gneiss. These outcrops are found scattering over an area of about 120 by 40 miles known as the Nigerian Minesfield, the most important of which are Kalato, Lireui, Rishi Hills, Tongolo Hills, Daya Allah, Gomber and Kwandonkaya. The tungsten deposits occur as detrital deposits, quartz veins, lodes and stockworks or impregnations. Cassiterite is found associated in most cases with wolframite. Other unimportant associated minerals are quartz, feldspar, mica, chalcopyrite, chalcocite, siderite, arsenopyrite, bismuth, stannite, beryl and fluorspar. It is only in the Lireui lode that galena, cerussite, blende, columbite and topaz have been found in any quantity. The distribution of wolframite is most irregular and sporadic and can only be profitably mined when the price is above 75 cents per unit of WO_3.

Wolframite and scheelite have been found at a number of places in South Africa, and many years ago scheelite was found in small quantity near Tsumeb, South-West Africa.

One of the very interesting deposits is at the Natas Mine, in the Kuisib Mountains, 140 miles east of Swakopund, South-West Africa. Individual crystals of scheelite reaching a weight of 12 pounds are found in a pegmatite and are accompanied by feldspar, mica, copper minerals, tourmaline, calcite, apatite and gold. The scheelite was probably introduced into the pegmatite at a very late date.

The Ottilie Mine belonging to the Krautzberg Mines (Pty.) Ltd. of Omaruru is at present the best developed.

Tungsten deposits also occur in Tanganyika Territory, Uganda and Egypt.

CUBA[45]

The tungsten deposits of the Isla de Pinos, Cuba, occur in the southwestern part of the island, near the Lomas de Siguanea. The dominant rocks of the district are fissile biotite and muscovite schists. The most abundant igneous rock is feldspar-quartz porphyry. The ferberite found in the quartz-tourmaline veins, which fill fractures in the schists, quartzite, and feldspar-quartz porphyry, is quite erratic in its distribution. A little scheelite has been found by alteration of ferberite. Besides the vein deposits there are plain deposits which however have not yet been prospected or tested. The tungsten deposits are found in an area about 12,000 feet long and 5,000 feet wide, but the most promising ones are localized in an area of about 6,000 by 2,800 feet. It has been estimated that the reserve of tungsten ore in sight amounts to about 55,000 tons containing about 750 tons of WO_3.

CANADA[55]

Tungsten minerals are found widely in Canada. Jolliffe enumerates 152 occurrences, of which many are of mineralogical interest only. A great many of the occurrences are gold mines in which scheelite is sometimes obtained as a by-product.

Nova-Scotia

"Tungsten occurs in small amounts at many places along the southeastern coast of Nova Scotia. The deposits are found in quartz veins that are mineralogically and structurally similar to the gold veins of the same region. In general, the quartz veins of this region are bedded with strongly folded Cambrian slates and quartzites which have been intruded by Silurian granite rocks. The tungsten mineralization appears to have been concentrated along the crests and troughs of steeply pitching folds."

New Brunswick

In New Brunswick, at Burnt Hill Brook in York County, wolfram is found associated with molybdenite, pyrrhotite, cassiterite, pyrites, mispickel, mica, topaz, and fluorite in quartz veins traversing argillites, not far from a granite intrusion.

Quebec

Scheelite has been found in several of the gold mines in the Province. Only very small shipments of scheelite have been made from such mines as Lamaque, Wood Cadillac and Sullivan Consolidated.

Ontario

Scheelite is found in several of the gold mines. The Hollinger Consolidated Gold Mines has constructed a mill at Timmins for recovering scheelite from its gold ores. Small shipments have been made from the Preston East Dome, McIntyre, Dome, Delnite, Little Long Lac gold mines.

Manitoba

Scheelite was found near Falcon Lake and in the Herb Lake area.

Northwest Territories

Tungsten had recently been produced on Outpost Island, Northwest Territory[59]. The Outpost formation has been classified as consisting of mineralized shear zones in micaceous quartzites. The mineralization consists of ferberite, associated with magnetite, specular hematite, probably ilmenite, pyrite, marcasite, bornite, chalcocite, covellite, molybdenite, powellite, chlorite, sericite and gold. Tungsten content averages 1 per cent and copper varies from 1 to 3 per cent. It is said that gold recovery more than pays operating expenses, so that the tungsten and copper concentrates represent profit. This deposit gives promise of being Canada's largest tungsten producer.

According to the Geological Survey of Canada, scheelite has been found in about 1,000 veins in the Yellowknife-Gilmour Lake Area.

Yukon

Placer scheelite has been found in some of the Yukon placer areas.

British Columbia[51]

"Occurrences of tungsten minerals are widespread throughout the Province. Tungsten is found in the Coastal areas, the Northern and Southern Interior and in the West Kootenay district.*

"Of the tungsten-bearing minerals, scheelite is by far the most abundant in British Columbia. Wolframite, the other common ore-mineral of tungsten, has been found at the Tungsten-Wolframite prospect in the Atlin area, at the Red Rose and Black Prince in the Hazelton area, and in the Sheep Creek area. Tungstic oxide minerals and stolzite, a lead tungstate, have been found in the Taylor prospect in the Cariboo district. Tungstite has also been found in the Reno Mine in the Nelson district. Powellite, which is a calcium molybdate and sometimes contains tungsten, commonly forms as an oxidation product of molybdenite in the presence of scheelite. Powellite occurs in some of the high-temperature replacement (lime-silicate) deposits of scheelite in the Southern Interior and West Kootenays. Other than scheelite, none of these minerals afford any promise of tungsten production from the deposits found so far.

In British Columbia scheelite is found in many different types of veins and in high-temperature replacement (lime-silicate) deposits. In the Bridge River area it is found in narrow, carbonate-stibnite veins at the Tungsten Queen and Tungsten King mines, and in gold-bearing quartz-veins in some of the gold producing mines of the district. At the Regal Silver mine near Revelstoke it is associated with lenses of heavy pyrite in quartz veins. In the Cariboo it is found in gold-bearing quartz veins variously associated with pyrite, galena, sphalerite and tetrahedrite. In the Telkwa-Hazelton area it occurs in lenticular quartz veins associated with apatite and orthoclase.

In the Nelson area, import scheelite deposits of the high-temperature replacement (lime-silicate) type were found in 1942. The deposits are in limestone and associated sediments close to contact with granite rocks. The mineralization is characterized by quartz, lime garnet, diopside, vesuvianite and in places pyrite and pyrrhotite; magnetite is apparently absent. In some places limestone beds have been completely and uniformly replaced by these minerals and the resulting rock is locally referred to as "skarn." Similar rock associated with scheelite is referred to as "tactite" in California and Nevada. Since the discovery of important quantities of scheelite in the Nelson area, particularly at the Emerald

---

* John S. Stevenson mentions 81 occurrences in Bull. No. 10 (Revised), British Columbia Dept. of Mines.

mine, numerous other discoveries in lime-silicate rocks have been reported from the southern part of the Province.

In common with the Western United States, British Columbia is part of that geologic unit known as the Cordilleran region which extends north-westerly and south-easterly along the westerly part of North America. The deposits responsible for the United States production of tungsten lie within this region, and it is therefore reasonable to expect somewhat comparable deposits in the part of the same region in British Columbia. Because of these favourable conditions, further prospecting for tungsten minerals within the Province, and the development of likely prospects might be expected to yield favorable results."

RUSSIA

In spite of its enormous expanse over eastern Europe and the northern half of Asia, Russia has few tungsten deposits and so far as is known those are comparatively small.

Descriptions about occurrences of tungsten in Russia are meager and confusing. The little that we know about the Russian tungsten deposit is contained in an excellent article on "Mining Development in Soviet Russia" by Cyril S. Fox.[40] To quote:

"There is some confusion in regard to the exact position of localities, which are given briefly as Trans-Baikal, where the boundaries of Eastern Siberia and Buryat Mongolia are somewhat involved. This is also partly true of places given as in the Altai, which may be Rudmy, Altai, Kalba and Gomey (alpine) Altai, where tungsten and tin ores occur in association with granite intrusions and which are difficult to fix, Oriat, Kazakh or West Siberia. . . . Workable occurrences of wolfram are being opened up in the Trans-Baikal area of East Siberia at Bukuka and Belukha; and it is presumed that these Trans-Baikal tin ores are to supply the smelter which has been projected in the Far Eastern Republic. Cassiterite and wolfram occur in the Far Eastern Republic—the former in the extreme north in the remote Chukotski peninsula, and the latter mineral at or near Ubinsk. . . . On the other hand wolfram specimens were on show from Kolyvan in the Altai (W. Siberia) Sargardon in Kazakh and a discovery is reported from near the copper mines of Kaunrad in central Kazakh and another from the Bostandyk mountains in Kazakh. . . . Prof. Smolin had reported several wolfram-bearing veins in a dozen places in the area between Sverdlovsk-Magnitogorsk and between Chelyabinsk and Zlatoust.

"Wolfram-bearing veins of the area southwards from Sverdlovsk near which is the Boerska deposit, through Chelyabinsk, to the Trebyi deposits east of Magnitogorsk, have proved of considerable interest, not merely from the importance of their possible usefulness . . . but also from a geochemical aspect. N. A. Elisseiev, as well as I. F. Grigoriev, working in the Rudmy Altai and Kalba Range, concluded that the ore-bearing characteristics of that region appeared to indicate direct genetical relationships with the nature of igneous intrusion in that area. A quietly cooling granitic intrusion, for example, was the most favorable for the deposition of tin and tungsten ores in cracks and veins (fissures) in the adjoining rocks. Thus a large granite massif which was connected with dykes, representing residual magma extruded from the granite, might be taken as the source of supply of the mineral veins, which were evidently connected with these dykes, and contained zinc-lead-copper, or silver-gold-copper, or yet again zinc-copper, respectively. However, in the scheelite occurrences of Buranovsky and Balkausky of the Trebyi tungsten ore area near Magnitogorsk, the best known of the scheelite deposits of Gumbeiko in the Chelyabinsk area of the South Urals, it has been noted by I. Stepanov that whereas the tungsten ore-bearing veins are connected with granite intrusions, the scheelite deposits are evidently confined to the apical part of the intrusive granite bosses and are in fact contact deposits. It is thus of particular interest to find that the scheelite from Lyangar, Uzbekistan, comes from a contact deposit, and it would appear that a search for wolfram is best restricted to veins in association with intrusive dykes, apophyses, from a granite, while scheelite deposits may be expected in contact with the granite massif itself."

OTHER EUROPEAN COUNTRIES

Tungsten ores are found in Austria, Czechoslovakia, France, Germany, Italy and Sweden, but their output is spasmodic and insignificant.

Tungsten Resources of the World

It is true that estimation of ore reserves in general is more or less guesswork, especially in the case of the estimation of tungsten reserves. But guesses are better than nothing; at least, they would give us, in this case, an indication of the relative importance of the tungsten-producing countries of the world.

Tungsten Resources of China*
(in metric tons, carrying 60% WO_3?)

Province	Tungsten Ore Reserve	Percentage in Total
Kiangsi	1,647,000	88.27
Hunan	51,100	2.76
Kwangtung	148,855	7.98
Kwangsi	17,911	0.97
Fukien	432	0.02
	1,865,798	100.00

* Yunnan excluded.

Tungsten Resources of China by Districts
(in metric tons, carrying 60% WO_3?)

Province	Localities	Principal Ore Minerals	Tungsten Ore Reserve	Data From
Kiangsi	Tachishan, Ch'iennan	Wolframite	104,600	K. C. Hsu
	Kueimeishan, Lungnan	"	214,600	"
	Sihuashan, etc., Tayu	"	490,600	"
	Pankushan, Anyuan	"	225,100	"
	Siaotungkeng, Tsungyi	"	46,500	"
	Changtienwu, Shangyiu	"	57,000	"
	Tiehshanlung, etc., Hueichang	"	46,900	"
	Shangping, Yutu	"	59,900	"
	Peshih, etc., Kanhsien	"	91,800	"
	Siaolung, Taiho	"	56,000	"
	Fuszushan, Hsingkuo	"	9,500	"
	Liangpichou, Suichou, Tayu	"	8,000	"
	Yachishan, Tsungyi, Nanking	"	237,000	"
	Total in Kiangsi		1,647,500	
Hunan	Peyunsien, Jucheng	Wolframite	7,000	Geol. Survey of Hunan.
	Yingtsuiyen, Ninghsien	"	12,000	" " " "
	Yaokangsien, Tzehsing	"	15,800	" " " "
	Others	"	16,300	" " " "
	Total in Hunan		51,100	
Kwangtung	Shuitung, Wengyuan	Wolframite	126,000	
	Tiehtingtou, Lochang	"	22,855	
	Total in Kwangtung		148,855	
Kwangsi	Limuhsiang, etc., Kungcheng	Wolframite	12,671	Geol. Survey of China
	Chuhohsiang, etc., Nantan	"	5,240	" " " "
	Total in Kwangsi		17,911	
Fukien	Nuhushan, Putien		432	
	Total in Fukien		432	
	Grand Total		1,865,798	

Tungsten Reserves of the World[41], China Excluded
(According to Hess with Modifications)

Country or Province	Amount Short Tons Carrying 60% WO_3	Country or Province	Amount Short Tons Carrying 60% WO_3
New Zealand	1,000	Peru	2,000
Tasmania	15,000	Bolivia	40,000
New South Wales	1,000	Argentina	5,000
Queensland	1,000	Brazil†	45,000
Northern Territory	5,000	England	2,000
Malay States	5,000	France	1,000
Burma	80,000	Spain	5,000
Tonkin	5,000	Portugal	20,000
Thailand	1,000	South Africa	1,000
Japan	1,000	Southern Rhodesia	2,000
Chosen	25,000	Miscellaneous‡	6,000
Russia	15,000		
United States*	80,000	*Total*	367,000
Canada	3,000		

References

1. Hess, F. L. and Schaller, W. T., "Colorado Ferberite and the Wolframite Series", *Bull. 583, U.S.G.S.* 37 (1914).
2. Information Circular No. 6821, *U. S. Bureau of Mines*, 6 (Jan. 1935).
3. Lindgren, W., "Mineral Deposits," p 121, 3rd Ed., McGraw-Hill Book Company, New York.
4. Jones, W. R., "Lectures delivered at Tavoy under the auspices of the Mining Advisory Board", Rangoon, p. 40 (1918).
5. Brown, J. C., and Heron, A. M., *Memoirs of the Geological Survey of India*, **XLIV**, pt. 2 (1923).
6. Hess, F. L., and Larsen, E. S., "Contact Metamorphic Tungsten Deposits of the United States", *Bull. 725-D, U.S.G.S.*, 255 (1921).
7. Jones, W. R., "Tin and Tungsten Deposits", *Trans. Inst Min. Metal , London*, 325 (1919 1920).
8. Brown, J. C., and Heron, A. M., *Memoirs of the Geological Survey of India*, **XLIV**, pt. 2, 242 (1923).
9. Hess, F. L , and Larsen, E. S., "Contact Metamorphic Tungsten Deposits of the United States", *Bull 725-D, U.S.G.S.*, 249 (1921).
10 Jones, W. R., "Tin and Tungsten Deposits, the Economic Significance of their Relative Temperatures of Formation", *Trans. Inst. Min. Metal., London*, (1919 1920).
11. Campbell, J. M , "Tungsten Deposits of Burma and their origin", *Econ Geol.*, (Sept. 1920), and "Lectures delivered at Tavoy", 2nd Series, (1919).
12. Brown, J. C., *Memoirs of the Geological Survey of India*, **XLIV**, pt. 2, 244 (1923).
13. Scrivenor, T. B , "The Geology of Malayan Ore Deposits", pp. 2-3, London, 1928.
14. Gannett, R. W , "Experiments relating to the Enrichment of Tungsten Ore", *Econ. Geol.*, 70-1 (Jan.-Feb., 1919).
15. Campbell, J. M., "Tungsten Deposits of Burma and their Origin", *Econ Geol.*, 521-2 (Sept., 1920).
16. Graton and McLaughlin, *Econ. Geol* , **XIII**, 83-86, (1918).
17. Roush, G. A., "Strategic Mineral Supplies", p. 147, (McGraw-Hill Book Company) New York, 1939.
18. Chung Yu Wang, "The Relation of Tectonics to Ore Deposits", *Bull. Geol. Soc. China*, **III**, No. 2, 169-181 (1924).
19. Kechin Hsu, "Geology of the Tungsten Deposits in Southern Kiangsi China", Thesis, University of Minnesota, 1941
20. Dunn, J. A., *Records Geol Survey India*, 73, pt. 2, 230-235 (1938).
21 Brown, J C., and Heron, A. M., "The Geology and Ore Deposits of the Tavoy District" *Memoirs of the Geol. Survey of India*, **XLIV**, pt. 2 (1923).
22. Dunn, J A., *Records Geol. Survey India*, 73, pt. 2, 244-5 (1938).
23. Scrivenor, J. B., "The Geology of Malayan Ore Deposits", p. 131, London, 1928.
24. Hess, F L. and Larsen, E S , "Contact Metamorphic Tungsten Deposits of the United States", *Bull 725-D, U.S.G.S.* (1921).
25. Kerr, P. F., "Geology of the Tungsten Deposits near Mill City, Nevada", *Bull. Nevada Bureau of Mines*, **28**, No. 2, (1934).
26. Kerr, P. F., "Tungsten Deposits at Silver Dyke, Nevada", *Bull. Nevada Bureau of Mines*, **30**, No. 5.
27. Kerr, P. F., "Tungsten Mineralization at Oreana, Nevada", *Econ. Geol* , **33**, No. 4 (1938).
28. Lemmon, D. M., and Dorr, J. V. N., 2nd , "Tungsten Deposits of the Atolia District San Bernardino and Kern Counties, California," *Bull. 922-H, U.S.G.S.* (1940).
29. Hess, F. L., and Larsen, E. S., "Contact Metamorphic Tungsten Deposits of the United States", *Bull. 725-D, U.S.G.S.*, 274-6, (1921).
30. Lemmon, D. M., "Tungsten Deposits in the Tungsten Hills, Inyo County, California", *Bull. 922-Q, U.S.G.S.*, (1941).
31. Wilson, E. D., "Tungsten Deposits of Arizona", *University of Arizona, Bull.*, **XII**, No. 2 (April, 1941).
32. Lovering, T. S., "Tungsten Deposits of Boulder County, Colorado", *Bull. 922-F, U.S.G.S.*, (1940) and "The Origin of the Tungsten Ores of Boulder County, Colorado", *Econ. Geol.*, 229-279 (May, 1941).
33. Wright, C. M., "Mineral Trade Notes", U. S. Bureau of Mines, 13-34 (Sept. 20, 1939).
34. Hess, F. L., "Some Unique Bolivian Tungsten Deposits", *Eng. Min. J.*, 492-499 (Sept. 24, 1921).
35. Rastall, R. H., and Wilcockson, W. H., "Tungsten Ores", pp. 70-71, Imperial Institute Monograph, John Murray Company, London, 1920.

---

*Based on paper "The Mineral Position of the U. S." by E. W. Pehrson, in *Mining and Metallurgy*, April, 1945, with the authors' calculations:

Commercial Reserves	21,600 tons
Submarginal Reserves	54,000 "
	75,600 tons (approx. 80,000 tons)

† Based arbitrarily on 30 years' supply of the 1944 production.

‡ Includes small outputs from such countries as Netherlands East Indies, Alaska, Canada, Mexico, the Scandinavian Peninsula, Germany, Czechoslovakia, etc.

36. Wright, C. W., *Minerals Quarterly*, U. S. Bureau of Mines, **III**, No. 3, 26 (July, 1940).

37. Rastall, R. H., and Wilcockson, W. H., *ibid.*, p. 39.

38. Rastall, R. H., and Wilcockson, W. H., *ibid.*, p. 43.

39. Bruder, C., "Canada has Tungsten Producer in Northwest Territories", *Eng. Min. J.*, 47–49 (May, 1942).

40. Fox, C. S., "Mining Development in Soviet Russia", *Trans. Min. Geol. Metal. Inst. of India*, **34**, pt. 2, 159-160. (August, 1938).

41. American Tungsten Association, pamphlet, (March, 1938).

42. Crawford, Arthur L., "The Tungsten Pipe of the Reaper Mine", *Proc. Utah Acad. Sci.*, **19/20**, 143-9 (1941–1943) published 1944.

43. Myasnikov, V. S., "Production of Synthetic Scheelite with Reference to its Origin in Nature", *Compt. rend. Acad. Sci. U.R.S.S.*, **30**, 412-14 (1941).

44. Kerr, Paul F., "Tungsten Bearing Manganese Deposit at Golconda, Nevada", *Bull. Geol. Soc. America*, **51**, 1378 (1940).

45. Page, Lincoln R., and McAllister, James F., "Tungsten Deposits Isla de Pinos, Cuba", *U.S.G.S. Bull. 935-D* (1944).

46. Haag, H. L., "Wolfram in Nigeria, "*Trans. Inst. Min. Met. (London)*, **LII**, 119-183 (1943).

47. Maclaren, Malcolm, "The Geology of East Pool Mine, Camborne, Cornwall", *Mining Mag*, **245** (May, 1917).

48. Dunn, J. A., *Trans. Min. Geol. Inst. India*, **36**, Pt. 1, 67-70 (1940).

49. Johnston, W. D. Jr., and Francisco Moacyr de Vasconcelos, "Tungstenio na Paraiba e Rio Grande do Norte", *Mineração e Metalurgia*, **VII**, No. 41, 247-260 (Nov., Dec., 1943).

50. Johnston, W. D. Jr., and Francisco Moacyr, "Scheelite in Northeastern Brazil" *Economic Geology*, **XL**, No. 1, 34-50, (Jan., Feb., 1945).

51. De Ment, Jack, "Ultraviolet Light in Mineral Prospecting", *Mining Congress J.*, p. 23-27, 37 (Jan., 1945).

52. Greenwood, R., "Effect of Chemical Impurities on Scheelite Fluorescence", *Econ. Geol.*, **38**, 56-64 (1943).

53. Warren, T. S., "Ultra Violet Light", Deco Trefoil (Denver Equipment Co.), March, 1944.

53a Rabone, P., "A Short Wave Ultra-Violet Prospecting Set for Fluorescent Minerals", *Bull. Inst. Min. Met. (London)*, No. 471, (March, 1945).

54. Munds, W. H., Ewoldt, H. B., and Cohen, C. J., "A Tungsten Find in North Carolina", *Eng. Min. J.*, 80-81 (Aug., 1944).

55. Stevenson, John S., "Tungsten Deposits of British Columbia", Bull. No. 10 (Revised), British Columbia Dept. of Mines (1943).

56. Kerr, Paul F., "Tungsten Mineralization in the United States", *Geological Society of America, Memoir 15*, March 9, 1946.

57. Knox, Newton B., "Tungsten Deposits of Peru", *Eng. Min. J.*, 95-98 (Aug., 1945).

58. Knox, Newton B., "Tungsten Deposits and Mining Conditions in Argentina," *Eng. Min. J.*, 90-93 (June, 1945).

Chapter III

The Ore Dressing of Tungsten

Since the First World War, the art of dressing tungsten ores has made immense strides. Before that period, and even as late as 1916, the primary comminution equipment consisted of gravity stamps, and neither stage grinding nor size classification had yet been well developed. Most of the mills were put up in haphazard ways and some of them appear as marvels of poor construction and bad practice. For instance, the Wolf Tongue concentrator in Boulder County, Colorado, did not adopt roll crushing until as late as 1913. In the Tavoy district, Burma, the ore was also crushed in gravity stamps even in 1916. Hence, in the light of present knowledge, it is not surprising that the average recovery of these early mills was as low as 60 per cent or even less.

The development of the contact deposits in Nevada and California during recent decades has given rise to certain milling problems, and resulted in the use of flotation. The comparatively heavy loss due to the sliming of scheelite during milling has commanded the attention of many investigators since 1937, both in America and Russia. The solution of these problems will eventually improve the percentage recovery in the milling of tungsten ores.

Each type of tungsten deposit is a problem by itself in the matter of selection of the proper method of concentration, depending on the tungsten mineral, its allied valuable minerals and its gangue constituents. The problem involves consideration of the physical characteristics of the minerals in the ore--their specific gravity, hardness and friability—as well as consideration of the intimacy of aggregation, size of mineral particles, and the condition of locked particles.

The presence of such minerals as pyrite, arsenopyrite, pyrrhotite, sphalerite, calcite, apatite, etc., as well as of tin, molybdenum and bismuth, bears on the successful milling of the ores and the production of a concentrate that is acceptable or marketable without undue price penalty. The process of milling is sometimes complicated by the fact that the subsidiary minerals—tin, molybdenum or bismuth—if present in sufficient amount in the ore, demand recovery as such.

Most tungsten deposits are of low grade. The lower limit of the grade of ore that can be concentrated profitably depends primarily upon the market value of the concentrate. For instance, 0.5 per cent WO_3 ore may not be profitably concentrated if the unit price of the concentrate is say $10, but it would become a valuable ore if the unit price is say $20. The great majority of the scheelite ores mined in the United States carry from 0.4 to 1.0 per cent WO_3; the Bolivian ores, 2.0 and even as high as 5 per cent; the Chinese ores, 1.0 of 3.0 per cent, averaging 2 per cent; the Mawchi ores (Burma) 1.5 per cent WO_3 and 2.0 per cent Sn.

The aim of most of the mills is to produce a concentrate containing at least 60 per cent WO_3. To attain this sometimes involves a lower recovery with some classes of ore. For instance, with scheelite ore, 60 to 65 per cent recovery is considered fair and an 80 per cent recovery, rather exceptional; with wolframite ore, an average 70 per cent recovery is fair, and 80 to 90 per cent recovery, exceptional. Attempts at a higher percentage recovery may yield a concentrate very much below 60 per cent WO_3.

As a general rule, the better the grade of mill feed, the better the percentage of extraction. However, it sometimes happens that a low-grade ore may be more valuable than one of higher grade because it is easier to concentrate and yields a higher recovery.

Beneficiation of wolframite, ferberite, hübnerite, and scheelite ores involves problems that have to be worked out in a laboratory. Experience has shown that results obtained by laboratory tests can usually be attained in full-scale commercial operations. Besides the usual common gangue minerals, such as quartz, feldspar, garnet, mica, sulfides, arsenides, apatite, calcite, and other carbonates associated with contact metamorphic ores, there are often valuable minerals, such as cassiterite, molybdenite, and bismuthinite. The milling problem of tungsten ore would thus become quite complex, involving as it does elimination of the associated gangue minerals and the recovery of the valuable minerals, if present in sufficient quantities to warrant such recovery.

The methods generally adopted for concentration of tungsten ores and for improvement of their concentrates are: gravity, flotation, magnetic, electrostatic, pneumatic, float and sink, roasting and leaching. The amenability to treatment of the ores or of their concentrates with respect to any of the methods or a combination of the methods depends upon the types of ores or concentrates and their associated minerals. The following table shows this clearly:

Materials for Treatment	Methods Used
1. Wolframite, simple ore	Gravity, flotation
2. Wolframite concentrate	Air tabling
3. Wolframite and cassiterite ore	Gravity, flotation, magnetic

4. Wolframite and scheelite concentrate	Magnetic
5. Wolframite, cassiterite and bismuth concentrate	Magnetic, leaching
6. Wolframite, scheelite and cassiterite ore	Gravity, flotation, magnetic and electrostatic
7. Wolframite and molybdenite ore	Gravity, flotation
8. Wolframite, arsenopyrite, pyrite and other sulfide ores	Gravity, flotation, roasting
9. Scheelite, simple ore	Gravity, flotation
10. Scheelite and cassiterite concentrate	Electrostatic
11. Scheelite, apatite, calcite ore	Gravity, flotation, leaching

To particularize the above, we may have the following:

I. Wolframite Ore
  (1) Wolframite-Molybdenite
    Flotation to separate the molybdenite
  (2) Pyritic Concentrates
    (a) Roasting and dressing over tables to remove the porous iron oxide.
    (b) Flash roasting and magnetic separation for removal of the magnetic oxide.
  (3) Wolframite-Bismuth
    Magnetic separation.
  (4) Wolframite-Tin
    Magnetic separation.
  (5) Wolframite-Tin-Bismuth
    Magnetic separation followed by leaching to separate bismuth from cassiterite.
    If the cassiterite is intimately coated or locked with iron, treatment with acid is necessary to render the wolframite-tin ores suitable for magnetic separation.

II. Scheelite Ore*
  "(1) Method 1
    (a) Extraction of the diluting, magnetic iron, garnet, epidote and other magnetic minerals by means of a Wetherill type magnetic separator, operating under a high potential.
    (b) Quick magnetizing roast, coating the pyrite particles with a thin film of magnetic oxide.

---

* Excerpts from paper by E. H. Burdick on "An Abstract Review of the Tungsten Industry in the United States with Notes on Some Metallurgical Problems Developed," read at the Annual Meeting of A. I. M. E., Feb. 9, 1942.

(c) Repass of the roasted material through the magnetic separator to remove the magnetized pyrite particles.
(d) Sweet roast of the magnetically cleaned concentrates to remove as far as possible the remaining sulfur.
(e) Return of the separator 'cutouts' to the mill circuit for regrinding and reconcentration.

"(2) Method 2
(a) Clean by flotation the table concentrates, removing the sulfides as completely as possible.
(b) Dry and remove the diluting magnetic minerals with a magnetic separator.
(c) If necessary, sweet roast the flotation-cleaned concentrates.

"In most cases, the elements presenting the most serious problem are molybdenum, bismuth and sulfur. Of the three, the removal of molybdenum, if present in the form of a chemical combination with tungsten and calcium (powellite type), presents the most difficulty and so far as known is not extractable except by chemical treatment. . . .

"Molybdenum, if present as molybdenite, or associated with the iron minerals, is removable by table concentration, supplemented by flotation or magnetic cleaning.

"Sulfur, if present as a sulfide, is removable by either magnetic, flotation or roasting treatment or a combination of the three. If as calcium sulfate, its removal, except chemically, is difficult or impossible.

"Bismuth content can usually be reduced by proper flotation treatment."

In the past tungsten ores have been beneficiated by hand-picking and gravity-concentration processes, such as jigging and tabling. These processes of concentration are applicable if the difference between the specific gravities of the tungsten mineral and the associated gangue minerals is sufficient. When the tungsten mineral is liberated by coarse grinding, recovery of tungsten may be high; but when fine grinding is necessary to unlock the tungsten mineral particles, the recovery is necessarily low, because of the loss in fines. To obviate the difficulties arising from fine grinding or from the narrow difference in specific gravity between the tungsten minerals and the associated gangue minerals, flotation is resorted to. Flotation thus serves as a useful adjunct to gravity methods by permitting a higher recovery of concentrates of an improved grade.

With regard to the employment of gravity concentration methods in beneficiating scheelite ores, the concluding remarks given by Mr. E. H. Burdick* are pertinent. They are worth quoting. In addition they may be construed as having a bearing on the beneficiation of wolframite ores.

"1. Average recovery on low-grade ores requiring grinding to minus 30

---

* *Ibid.*

mesh will not exceed 70 per cent and more often will be 60 per cent or less, depending on the grinding required to free the tungsten minerals.

"2. Average recovery on coarse scheelite ores of from 1½ to 3 per cent and requiring grinding to minus 16 mesh will not exceed 90 per cent, the recovery factor being modified by the character of the ore gangue.

"3. That in all scheelite ores, and particularly those of garnet base, the slimes loss in table concentration accounts for from two to five times the loss in sand tails.

"4. That the methods used in the fine grinding operations have a marked influence on recoveries which can be attained, and that roll crushing, wherever adaptable, produces materially less ultimate sliming than ball or rod mill reduction to the same maximum mesh.

"5. That the recoveries now attainable by gravimetric methods preclude the successful development of large tungsten reserves and that if average recoveries could be increased to 85 to 90 per cent, tungsten production would then rest on a solid footing and take a permanent place in the mining industry, and thereby a reliable domestic supply of tungsten would be made available to meet all national needs.

"6. That there is an urgent necessity for the standardization of laboratory chemical methods for the correct determination of small amounts of tungsten and associated metals and elements in ores and products.

"As all bear on the prime factor of recovery, research in the following fields is suggested:

"(a) Methods of grinding to produce a minimum of fine material.

"(b) Methods for positive classification by size of the concentrating table feed.

"(c) What modification, if any, of the mechanical features of gravity tables is necessary to best accomplish increased recovery.

"(d) Secondary treatment of both slime and sand tailings.

"(e) Chemical laboratory practice."

GRAVITY CONCENTRATION

Present milling practice for tungsten ores is characterized by stage crushing and sizing. The fundamental principle to guide the designer of the milling plant is that the reduction in particle size be so controlled that removal of values is accomplished as soon as they are released from the matrix. High recovery is thus conditioned by the successful performance of this procedure.

Crushing and Grinding

Stamps have become obsolete for crushing tungsten ores. Jaw crushers or grating crushers are now used for primary crushing. The crushed product, which may or may not be screened, goes to rolls. For grinding to finer sizes, roll-mills or rolls may be used. For grinding table tailings or classifier products, grate-type ball mills may be employed to further liberate all the mineral. Rolls give less sliming than ball mills; however, sliming in ball mills is lessened by using ball mills with a large diameter and short length and by using an excess amount of water.

Classification

To prevent excessive sliming, the ground products must be classified thoroughly before being concentrated. The importance of making a clean-slime separation must be emphasized. Each sized product is separately treated in a series of machines appropriate for the task as well as consistent with economy. It becomes apparent that the proper selection and appropriate placing in the circuit of screens, hydraulic classifiers, *e.g.*, Akins, and settlers, *e.g.*, Callow cone, is a matter of importance in getting high recovery.

Jigging

The types of jigs adopted in coarse jigging are evenly divided between Hartz and Richards pulsating jigs. Generally "coarse" jigs make three products: concentrate, hutch, and tailing; "fine" jigs give two products: concentrate and tailing. In the absence of "fine" jigs, tailings from "coarse" jigs are reground by rolls, and after screening are treated on "coarse" tables.

Tabling and Slime Treatment

Various types of tables, such as the Card, James, Isbell, Deister, Wilfley and Overstrom, have been adopted in the concentration of middlings or tailings from the jigs, after regrinding with or without classification. The sand tables make three products: concentrate, middling and tailing. The middling is circuited for separate treatment, or reground. The "coarse" from the tailing, after being passed through a hydraulic classifier or settler, may be reground in rolls or ball mills, and retreaded on tables, and the slime may be treated on slime tables, after thickening. In general, concentrates from slime tables are low-grade.

In the past Monell tables, Frue vaners and canvas tables have been used for slime treatment but during recent years they have been superseded by flotation. In the treatment of slime it is still a problem how to attain a higher recovery and to bring the grade of the concentrate up. The treatment of tailings and slimes by flotation will be discussed later.

Dewatering

Mechanical thickeners are used for dewatering the pulp. Dewatering serves two purposes: one is to enable the pulp to be handled more efficiently, and the other is to reclaim the mill water for further use.

FLOTATION

The application of flotation to the beneficiation of tungsten ores has become significant only during the last few years. Among those who have made contributions to the study of this problem are E. S. Leaver, M. B. Royer, J. Bruce Clemmer, R. G. O'Meara and Oliver C. Ralston (all of the U. S. Bureau of Mines), O. A. Deminova, S. Gulyayev, F. Na. Belash, O. V. Pugina, B. I. Rosov, and G. A. Miosnikova (Russian investigators), E. H. Burdick, M. Winkler, Wm. T. MacDonald,* Blair Burwell, Carl M. Dice of the National Reconditioning Co., and D. C. Laren. The results of their investigations have given impetus to the adoption of flotation as a useful adjunct to table concentration for the treatment of tailings, slimes or the high-sulfide concentrates from the tables, as well as to treating low-grade tungsten ores, tin-wolfram ores and particularly scheelite ores from contact-metamorphic deposits.

The problems of the flotation of tungsten minerals are those of the flotation of non-sulfide ores. Non-sulfide flotation relies upon the use of some derivatives of the fatty acids to float the useful minerals, as well as upon the proper selection of reagents to depress the gangue. For the removal of sulfide minerals, which are often found associated with tungsten ores and which sometimes contaminate the slimes, tailings and concentrates from the concentration tables, the usual xanthate collectors such as reagent 301, or Aerofloat flotation reagents such as Aerofloat 31, reagent 238 and reagent 242, are used.

The following reagents are generally used for tungsten flotation:

Collectors. Fatty acids and soaps are almost universally used for the flotation of the tungsten minerals. Oleic acid and sodium oleate are typical of the collectors used. When used in conjunction with an alkaline reagent such as caustic soda, soda ash or sodium silicate, they give a satisfactory separation of scheelite from quartz. Fatty acids are commonly fed to the circuit as an emulsion which appears to shorten the conditioning time required, and give a more accurate control of reagent addition. Recently much experimental work has been carried out on the flotation of scheelite using "Orso", a sulfonated fatty acid, which is added to the circuit as a dilute water solution. While having considerable merit in the flota-

---

* See References at the end of this chapter.

tion of scheelite, this reagent does not appear to be so effective for the flotation of wolframite.

According to S. A. Falconer and B. D. Crawford: "Some operations have reported good results with soaps such as saponified linseed fatty acid, or sodium oleate. At one property, sulfonated castor oil has been used as the promoter (collector). Reagent 712 a water-soluble fatty acid of vegetable origin has also shown some promise as a promoter for scheelite. In general, the quantities employed range somewhere between 0.25 to 1.75 pound per ton of ore. Improved results are usually obtained by staging the promoter and frother, rather than adding them all at one time ahead of flotation."

Frothers. Most of the collectors used for the flotation of tungsten minerals possess frothing properties to some degree. The use of oleates or other soaps is often limited by the excessive amount of froth produced. "Emulsol X-1," alcohols, and cresylic acid are commonly employed with the fatty acids. "Emulsol" is an excellent frothing agent which exhibits little or no collecting properties. It may be used in acid or alkaline circuits with equal effectiveness. Cresylic acid is commonly used when it it is desired to stiffen the froth. Best results are obtained by adding the reagent in stages throughout the circuit. According to S. A. Falconer and B. D. Crawford: "Enhanced results are usually obtained if an auxiliary promoter (collector) and froth modifier is used in conjunction with the scheelite promoter. Certain types of wetting agents, such as Aerosol OT (di-octyl sulfosuccinic acid-sodium salt), an anionic-type wetting agent, has been found to be quite effective for this purpose. Auxiliary promoters or froth modifiers of this type give a 'lacy' type of froth texture, which for most ores is an essential to securing better selectivity. Amounts used usually range from 0.10 to 0.30 pound per ton. In the Cyanamid laboratory it has been found that particularly good results are obtained with these reagents when used in conjunction with quebracho.

"In some instances, the promoter and froth modifier used for floating scheelite, give sufficient amount of froth and no additional frother is necessary. However, some ores may require a frother; du Pont frother B-23, frother B-48, and cresylic acid seem to be preferred for this purpose.

"In general, the same reagent used to float scheelite works well on ferberite, wolframite and hübnerite, but some modifications in quantities of reagents and in the flotation procedures itself usually are necessary. Wolframite is reported to be less readily floatable than scheelite but slightly more floatable than ferberite. Hübnerite is less readily floatable than wolframite."

Modifying and Depressing Reagents. Mineral acids such as sulfuric, phosphoric, or hydrochloric are sometimes used in depressing gangue minerals. Sodium silicate in an alkaline circuit is a valuable reagent for depressing various silicate gangue minerals, and to some extent, calcite as well. The alkalinity of the pulp should be in the pH range of 9.5 to 10.5. While the effect of this reagent on scheelite is small, it exerts a pronounced depressing action on wolframite, ferberite and hübnerite. Ordinarily only small quantities of silicate can be tolerated in wolframite circuits. Acidified dichromate is also an effective depressant for silica. A combination of sulfuric acid and sodium dichromate may be used for the depression of calcite and certain other carbonates. Short-chain organic acids such as formic acid or lactic acid, are commonly used in depressing apatite, which is so often found associated with scheelite ores.

Slightly acid circuits are preferred for the flotation of ferberite. The presence of a metal salt, such as manganese sulfate, in such circuit, helps to prevent the depression of ferberite by acids.

Aero Brand or sodium cyanide is used to depress unwanted sulfides during the flotation of the scheelite. Quebracho or tannin is used for the depression of calcite and dolomite.

Water Hardness

Water hardness is mainly due to the presence of calcium bicarbonate and calcium sulfate. These salts require a larger consumption of oleic acid than necessary, since they react with the oleic acid to form an insoluble calcium salt before the oleic acid has an opportunity to react with the scheelite surface. Their removal can be accomplished by the lime-soda process, the former removing the bicarbonate and the latter the sulfate.

Tungsten Ore Flotation

The treatment of this subject is based upon the pioneer work done by J. Bruce Clemmer and R. G. O'Meara.

For the flotation of the tungsten minerals, oleic acid and sodium oleate are commonly used. The siliceous gangues are usually depressed with sodium silitate. For depression of apatite, short-chain organic acids, such as formic and lactic acids, or mineral acids are used. Carbonates and fluorite can be depressed by a metal salt-silicate combination, such as copper sulfate and sodium silicate. In addition, this metal salt-silicate combination can retard flotation of apatite as well. Starch, glue or lactic acid is effective as a mica depressant.

Scheelite Flotation. (a) Experiment with a scheelite ore, containing quartz and apatite as gangues.

The use of oleic acid and sodium oleate in an alkaline circuit is effective in floating the scheelite. The quartz was depressed by a small amount of silicate. A final cleaning with formic acid depressed the apatite. Other acids such as hydrochloric, nitric, sulfuric, or sulfurous may be used to depress apatite.

(b) Experiment with a scheelite ore, containing 3.62 per cent WO_3 and 0.636 per cent phosphorus, associated with gold, arsenopyrite, mica and quartz.

The arsenopyrite was first floated in an acid circuit with the customary xanthate collectors. The scheelite was then floated with oleic acid and sodium oleate. The rougher froth was cleaned with sodium silicate to depress quartz and mica. A final cleaning with lactic and formic acids depressed the remaining mica and apatite. An alkaline circuit is preferable when phosphorus is absent, but an acid circuit is necessary when phosphorus is present.

For conditioning the pulp, copper sulfate was used. Other heavy-metal salts, such as copper nitrate and copper ammonium hydroxide, are equally effective.

The results are shown in the following table:

Flotation of a Contact Metamorphic Scheelite Ore, 65-mesh

Product	Weight (per cent)	Assay (per cent)			Per cent of total	
		WO_3	P	S	WO_3	P
Sulfide concentrates	16.0	3.74	0.082		7.0	10.7
Scheelite concentrates	7.8	74.10	.022	0.03	68.2	1.4
Middlings	11.8	14.64	.249		20.3	24.1
Tailings	64.4	.60	.121		4.5	63.8
Composite	100.00	8.49	.122		100.00	100.00
Feed		8.54	.137	5.27		

Reagent	Pound per ton of crude ore				
	Sulfide rougher	Scheelite			
		Conditioner	Rougher	Cleaners	
				1	2
K-amyl xanthate	0.40				
Aerofloat	0.32				
Copper sulfate		0.8			
Sodium silicate			1.00	0.25	0.20
Oleic acid			0.96		
Sodium oleate			0.20		

Ferberite Flotation. The ore under test was a second-grade jig concentrate from a gravity mill treating a Colorado ferberite ore, which contains only small amounts of sulfides and apatite. The results of this test are shown in the following table:

Flotation of Second-grade Jig Concentrates, 150-mesh

Product	Weight (per cent)	Assay (per cent)			Per cent of total	
		WO_3	P	S	WO_3	P
Concentrates	38.3	62.38	0.010	0.031	76.7	20.9
Middlings	28.8	23.96	.032		22.1	50.3
Tailings	32.9	1.10	.016		1.2	28.8
Composite	100.00	31.15	.018		100.00	100.00
Feed		31.20	.022	.019		

Reagent	Pound per ton of crude ore			
	Rougher	Cleaners		
		1	2	3
Oleic acid	0.88			
Sodium oleate	.35			
Acid dichromate	.05	0.15	0.25	0.30

Short-chain organic acids, such as lactic or formic acid or acidified dichromate, which was used in this case, are effective depressants for siliceous gangues. In certain ores in which the ferberite mineral is sensitive to depression by acid, the introduction of a small amount of a metal salt, such as manganese sulfate, renders the mineral less sensitive.

Wolframite Flotation. Wolframite is slightly more floatable than ferberite. The reagents used for ferberite ores act similarly on wolframite ores. The results of a typical test on a high-grade Washington Wolframite ore, which assayed 28.69 per cent WO_3 0.015 per cent phosphorus and 0.002 per cent sulfur, are given in the following table. The slightly acid circuit was preferred.

Flotation of a High-grade Wolframite Ore, 150-mesh

Product	Weight (per cent)	Assay (per cent)			Per cent of total	
		WO_3	P	S	WO_3	P
Concentrates	34.5	70.92	0.013	0.01	89.4	29.6
Middlings	21.7	12.54	.027		10.0	38.6
Tailings	43.8	.39	.011		.6	31.8
Composite	100.0	27.36	.015		100.0	100.0
Feed		28.69	.015	.002		

Reagent	Pound per ton of crude ore		
	Rougher	Cleaners	
		1	2
Oleic acid	0.96		
Sodium oleate	.40		
Acid dichromate	.05	0.10	0.15

Hübernite Flotation. Hübernite is more flotable than wolframite. Reagents that are satisfactory for ferberite or wolframite ores can be used with hübernite ores. The results of a test on an Arizona hübernite ore, assaying 4.20 per cent WO_3 and 0.005 per cent phosphorus, are shown in the following table. In this case butyl alcohol was used as frother.

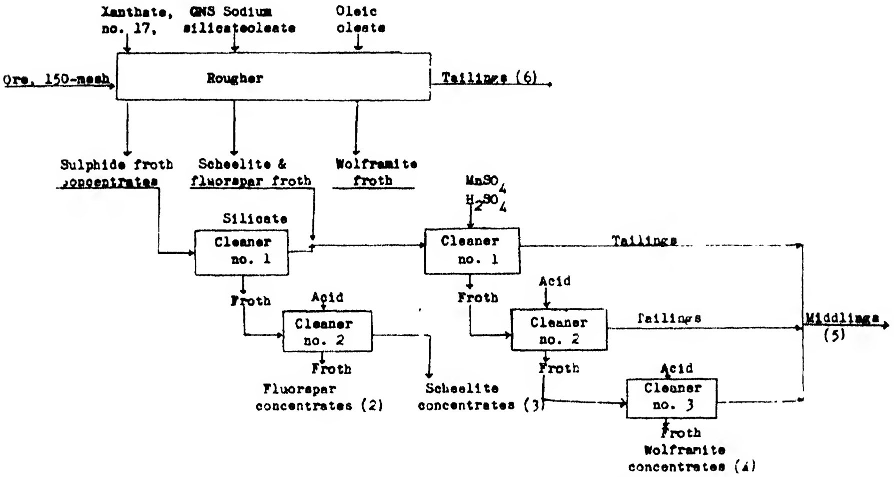
Complex Ores. The tungsten minerals, arranged in the order of increasing flotability, are ferberite, wolframite, hübernite and scheelite. From this one might expect that scheelite could be separated from wolframite. This separation has been made. Although such a separation would not be advantageous on tungsten ores in which scheelite and wolframite were the only readily floatable minerals, it might be necessary to make the separation to obtain marketable products if the ore contained other floatable minerals, such as fluorspar. The fluorspar and scheelite would be concentrated into one product and the wolframite into another. Retreatment of the fluorspar-scheelite product would yield a fluorspar concentrate and a scheelite concentrate.

Flotation of Arizona Hübnerite Ore, 150-mesh

Product	Weight (per cent)	Assay (per cent)			Per cent of total	
		WO_3	P	S	WO_3	P
Sulfide concentrates	4.2	1.31	0.016		1.4	8.7
Concentrates (hübnerite)	5.3	71.56	.012	0.043	90.2	8.2
Middlings	1.2	10.24	.015		2.9	2.3
Tailings	89.3	.26	.007		5.5	80.8
Composite	100.0	4.20	.008		100.0	100.0
Feed		4.25	.005			

Reagent	Sulfide	Hübnerite		
		Rougher	1	2
X-amyl xanthate	0.25			
Sodium silicate	.65			
Butyl alcohol	.14			
Oleic acid		0.40		
Sodium oleate		.10		
Acid dichromate				0.25

An ore was received from the Springvale mining district of Washington which assayed 1.48 per cent tungstic oxide and 0.009 per cent phosphorus. The tungsten was present as wolframite and scheelite associated with sulfides, and the gangue was composed mainly of quartz and mica. Other associated minerals were fluorspar, calcite, ankerite, apatite, and tourmaline. The complex nature of the ore and the low tungsten content made testing difficult, but the results of several tests showed that the ore could be concentrated by flotation. A typical test is given in the following flow sheet.



Treatment flow chart of a complex tungsten ore.

Flotation of Complex Tungsten Ore, 150-mesh

Product	Weight (per cent)	Assay (per cent)			Per cent of total WO_3
		WO_3	P	S	
Sulfide concentrates	1.9	2.09			2.7
Fluorspar concentrates	2.4	1.53			2.5
Scheelite concentrates	.5	59.85	0.051	0.020	20.2
Wolframite concentrates	.9	68.32	.020	.055	41.5
Middlings	5.6	8.44			32.0
Tailings	88.7	.02			1.1
Composite	100.0	1.48			100.0
Feed		1.48	.009		

Laboratory experiment has also shown that separation of scheelite from wolframite by flotation can be accomplished by conditioning the pulp with quebracho extract, using oleic acid as collector and frother for scheelite. At a pulp temperature of 20° the separation was found to be fair, while at 40° the flotation of the scheelite from wolframite was abrupt and fairly complete.

As an example of the treatment of complex scheelite ore by flotation in actual practice, mention may be made of the flotation mill recently erected by the United States Vanadium Corporation near Bishop, California. This mill is capable of treating 1,300 tons of ore per day. The scheelite ore, containing as accessories molybdenite and copper-silver minerals, is ground to approximately 90 per cent of minus 60 mesh and goes to the flotation machines at pulp density of 25 per cent solids.

"Each flotation section consists of three 10-cell, 18-in impeller Mineral Separation Type Stearns-Roger flotation machines. Sodium silicate, pine oil, and xanthatate are added and a bulk concentration containing 20 per cent MoS_2, 20 per cent copper, and 30 oz of silver is removed. This bulk concentrate goes to a cleaner circuit, where the sulfide flotation reagents are removed with steam, and the molybdenite and copper-silver are separated in a cyanide solution which depresses the copper-silver.

"Following the first sulfide flotation cells, the ore pulp is divided into the two remaining banks of cells, in which cresylic acid, Emulsol, and sodium oleate are added to float scheelite, and the flotation tailings pass to the tailings launder over pilot tables."

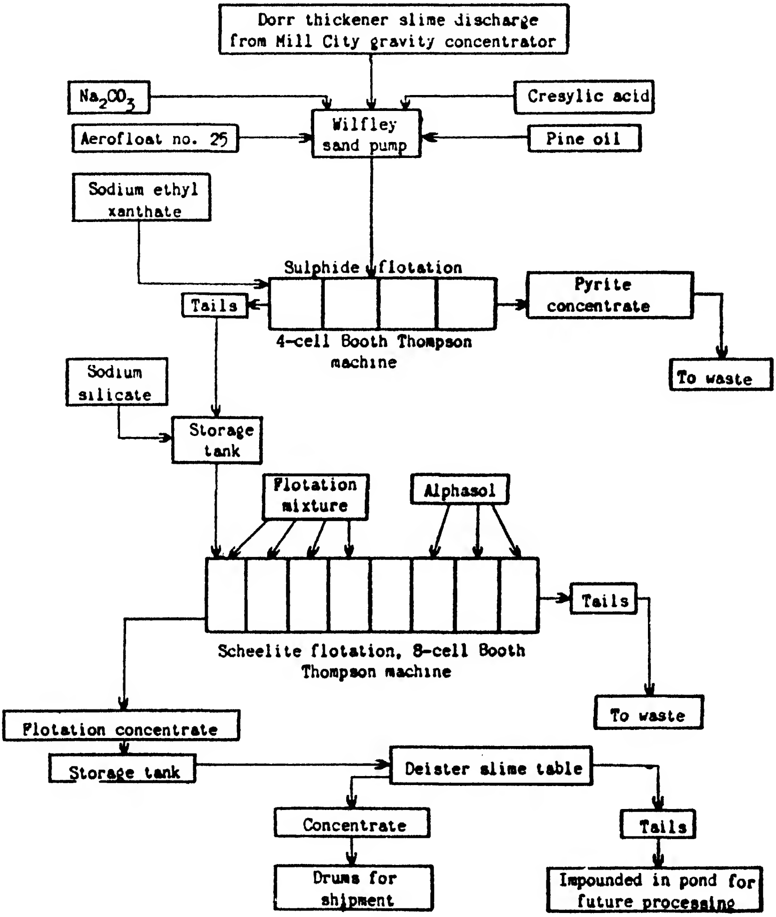
As a result of the study made by E. S. Leaver and M. B. Royer on the flotation for recovery of scheelite from slimed material (U. S. Bureau of Mines, Tech. Paper 585), the Nevada-Massachusetts Co. has built a 75-ton-per-day pilot flotation plant at Mill City, Nevada. The figure on p. 123 shows the process.

The pulp from the Dorr thickener in the gravity concentration plant, which still contains 0.5 per cent WO_3 and may otherwise go to the waste dump, is lifted to the head of the flotation plant. "The soda ash, Aerofloat, cresylic acid, and pine oil are added in a water solution to the pump and are thus well mixed before they reach the sulfide flotation unit. The sodium ethyl xanthate, in a 10-per cent solution, is added directly to the head box of the sulfide flotation machine. No attempt is made to attain a tailing free of sulfides as the scheelite loss would be too great under such operation. The sulfide float is merely to remove as much of the sulfide material as possible with a minimum loss of scheelite. The sulfide concentrate contains 0.1 to 0.2 per cent WO_3 and is wasted in the present scheme of operation.

"The tailing from the sulfide flotation machine passes to a tank where the sodium silicate is added. The tank provides a means for maintaining a constant feed to the scheelite flotation unit. Addition of sodium silicate was tried prior to sulfide flotation, but experience proved that this method was less effective and that larger amounts of the sodium silicate were needed than when it was added just before scheelite flotation.

"The flotation reagents for the scheelite flotation circuit are added from a disk-type reagent feeder. Regulated amounts of the reagent mixture are added to each of the first four cells of the eight-cell unit. The last three cells of the unit are treated with a frother booster to aid in floating most of the remaining particles of scheelite in the pulp.

"The collector and frothing mixture added to the first four cells comprises oleic acid, Emulsol X-1, B-22, and ethylene dichloride, in proportions of one-third, one-third, one-sixth, and one-sixth, respectively. The last reagent is merely an addition agent to make the X-1 sufficiently mobile to flow into the cells in cold weather, as X-1 becomes very viscous below 0°. During warm weather the dichloride may be eliminated.



Flow chart of 75-ton flotation plant at Mill City, Nevada, for recovering scheelite from slime.

"Reagents must be added to each cell instead of the head box, owing to the difficulty of maintaining a properly flowing froth in successive cells By adding Alphasol,* marketed by the American Cyanamid Co., to the

---

* C. M. Dice: "This reagent is sprayed onto the froth as a very weak solution in order to drop some gangue from the froth."

last three cells, a final extraction of scheelite is made without adding the expensive reagent mixture needed in the first part of the scheelite flotation.

"Control of the pH of the pulp water within narrow limits is the main factor in successful recovery of scheelite by the flotation reagent mixture described. A minimum pH of 9.0 and a maximum one of 9.5 have been determined by the flotation results obtained over a period of several months. The correct pH is maintained by proper additions of soda ash to the pump lifting the pulp to the flotation machine.

"When the pH is below 9.0 the froth tends to carry siliceous material in addition to scheelite and some calcite. Higher pH than 9.5 has such a pronounced effect on froth subsidence that an excessive consumption of reagents for floating is necessary to maintain a freely flowing froth. These pH limits appear to provide the proper balance for successful flotation.

"The scheelite flotation concentrate may range in grade from 6 to 20 per cent WO_3, depending on the mill feed supplied to the flotation plant and the operation of the scheelite flotation machines. The flotation concentrate may be expected to average 10 to 15 per cent WO_3, with a maximum of 20 per cent WO_3 under the best flotation conditions.

"As the concentrate from flotation is too low in WO_3 for marketing, a Deister slime table is placed in the circuit to raise part of the flotation concentrate to a satisfactory shipping grade. The 6- to 20-per cent WO_3 flotation concentrate comprising the feed to the table yields a concentrate ranging from 50 to 65 per cent WO_3.

"The results of the various reagent combinations indicate that the most satisfactory approximate reagent concentrations, in pounds per ton of dry slime, are: Oleic acid, 0.75; X-1, 0.75; Na_2CO_3, 10.0; Na_2SiO_3, 1.2; B-22, 0.35; Alphasol, 0.40; and enough ethylene dichloride to provide a mobile solution of X-1 and oleic acid in winter. The dichloride may be eliminated in hot weather."

Large-scale commercial treatment by flotation of high-sulfur tungsten concentrates from gravity concentrators may be exemplified by the Mawchi Mine Mill, Burma, and the mill of Lincoln Mines, Kiko, Nevada.

For the flotation of low-grade scheelite ores, S. A. Falconer and B. D. Crawford gave the following example: A low-grade ore analyzing 0.47 per cent WO_3 and containing scheelite, associated with the principal gangue minerals, epidote, garnet, quartz and calcite, was subjected to flotation following grinding to minus 65-mesh, which provided effective liberation of the scheelite from the gangue.

In the treatment of this ore, the use of optimum quantities of soda ash and sodium silicate was effective in securing selectivity when floating the scheelite with a combination of reagent 708 and oleic acid. Frother B-48 was of benefit in securing the desired type of froth.

The results obtained in a typical test on this ore are shown in the following table:

Typical Test on Ore Containing 0.47 Per Cent WO_3

Product	Metallurgical Results (per cent)			Reagents (lb per ton ore)				
	Weight	WO_3	Recovery WO_3	Soda Ash	Sodium Silicate	R-708 Oleic*	R-708	B-48
Feed	100.00	0.472	100.00	10.0	4.0	0.24	0.48	0.13
Cleaned concentrate	0.62	59.74	78.4					
Cleaner tailing	1.39	3.93	11.2					
Rougher concentrate	2.01	21.14	89.6		1.5		0.08	0.02
Rougher tailing	97.99	0.05	10.4					

* R-708 Oleic refers to equal weight mixture of these reagents.

Points of addition of reagents as follows:

Soda ash: to grind.

Sodium silicate: 4.0 lb per ton to conditioner (4 min. contact) prior to rougher float; 1.5 lb per ton to cleaner float.

Reagent 708, oleic acid mixture: to conditioner prior to rougher float.

Reagent 708: 0.08 lb per ton to conditioner prior to rougher float;
0.40 lb per ton staged to rougher float;
0.08 lb per ton to cleaner float.

Frother B-48: 0.10 lb per ton to conditioner prior to rougher float;
0.03 lb per ton to rougher float;
0.02 lb per ton to cleaner float.

Time of treatment: 4 min. conditioning of rougher float feed;
12 min. rougher float;
3 min. cleaner float.

pH Rougher float: 10.5.

Another typical-low-grade tungsten ore that responded well to flotation contained about 0.40 per cent WO_3 in the form of scheelite, associated with quartz, garnet, epidote and carbonate. Mineralization was relatively coarsely disseminated and 65-mesh grinding provided sufficient liberation for flotation separation. Typical results obtained in the testing of this ore are shown in the following table:

Typical Results on Ore Containing 0.40 Per Cent WO_3

Product	Metallurgical Results (per cent)			Reagents (lb per ton ore)					
	Weight	WO_3	Recovery WO_3	Soda Ash	Sodium Silicate	Quebracho	R-708 Oleic*	Aerosol 18	Frother B-23
Feed	100.00	0.44	100.00	8.0	1.0	0.30	0.50	0.55	0.03
Cleaner concentrate	1.11	34.33	87.0						
Cleaner tailing	8.17	0.48	8.8						
Rougher concentrate	9.28	9.61	95.8						
Rougher tailing	90.72	0.02	4.2						

* R-708 Oleic refers to equal weight mixture of these reagents.

Points of addition of reagents as follows:

Soda ash: To grind.
Sodium silicate: To conditioner (10 min. contact) prior to rougher float.
Quebracho: To conditioner prior to rougher float.
R-708 Oleic: Staged to rougher float.
Aerosol 18: Staged to rougher float.
Frother B-23: To conditioner prior to rougher float.
Flotation time: Roughing, 11 min; cleaning, 3 minutes.
pH Rougher float: 10.1.

The Mawchi Mine Flotation (after Denyer)

"Concentrates which are too fine for treatment by the Murex process are passed to the flotation plant for removal of the sulfides. A rather low grade concentrate is fed to the cells, and the sink, freed from sulfides, is brought up to the desired state of concentration on tables.

"Coarse and fine concentrates are treated in separate cells in batches of 9 cwt. Reagents are used as shown in the following table:

Reagent	Coarse and retreatment (lb per ton)	Fine (lb per ton)
Pine oil	0.23	0.18
Creosote	0.49	0.39
Sodium-ethyl-xanthate	0.05	0.04
Sulfuric acid	0.73	0.49

"In charging, the cell is first half filled with water and the ore and reagents are added. After a period of conditioning, the cell is topped up and the process completed as rapidly as possible to minimize the formation of fines by the impeller. The float from the first treatment is retreated to recover any cassiterite and wolfram which may have escaped with the froth. The float from the treatment cell goes to waste and the sink is returned to the coarse flotation feed. The sink from the first treatment passes to settling tanks, and slimes in the overflow are settled and treated in a concave buddle. The settled concentrate is treated on a table which gives a final concentrate and a middling, which is dewatered and re-treated on further tables. Concentrates are dried and bagged and all tails and over-flows are returned to the mill circuit."

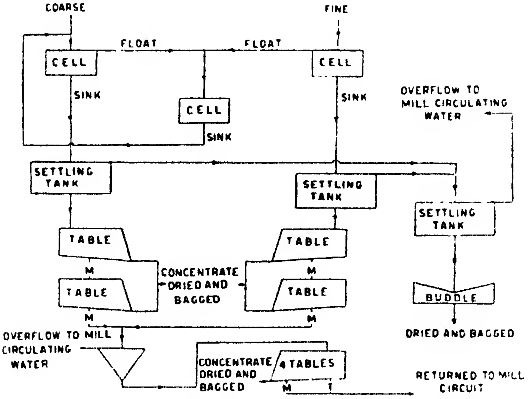
The figure below shows the flow sheet of the flotation plant:

The Lincoln Mines Flotation (after Burdick)

"Table concentrates containing fifty per cent or over of pyrites, are float-cleaned under the following procedure:

"With a batch cell charge of 800 pounds, the following reagents are added:

Z-6 Xanthate	2000 ml
$CuSO_4$	240 g
Pine Oil (Yarmouth F)	200 ml



Flowsheet of flotation plant.

"Conditioned 5 to 15 minutes and the froth pulled clear and clean. The air is then dropped and further reagents added:

$CuSO_4$	50 g
Z-6	500 ml

"Conditioned 1 to 5 minutes and the froth pulled clear and clean. The air is again dropped and reagents added:

H_2SO_4 (Coml).	500 ml

"Very short conditioning period. This is the final froth and pulled as clean as possible."

The results obtained by the Russian investigators on the flotation of tungsten minerals may be summarized as follows:

(a) **According to Gulyayev.** The scheelite table concentrates must be crushed to 60 per cent 200 mesh. The best results were obtained with application of the following reagents:

Liquid glass	400 gr/t
Acidol	188 " "
Sodium oleate	320 " "

(b) **According to Deminova.** Experiments were made on a scheelite-chalcopyrite ore containing 0.12 per cent WO_3. The gangue minerals are mainly feldspars, calcite and sphalierite. The copper-tungsten concentrates obtained by tabling were first crushed to −60 mesh and then were treated in flotation cells with butyl xanthate and pine tar to float the copper minerals. For flotation of the scheelite, oleic acid, sodium oleate and sodium silicate were used. Calcite, found as diluent in the concentrate, may be removed with 10 per cent hydrochloric acid solution. The following tables give the results of the experiment.

Products of tabling	Output (%)	Content (%)		Extraction (%)	
		WO_3	Cu	WO_3	Cu
Collective concentrate	12.12	0.65	9.45	79.61	81.82
Tails	87.88	0.02	0.29	20.39	18.18
All of Ore	100.00	0.10	1.40	100.00	100.00

Products of flotation	Output (%)	Content (%)		Extraction (%)	
		WO_3	Cu	WO_3	Cu
Copper concentrate	51.43	0.18	21.65	11.43	99.56
Tungsten concentrate	4.21	15.14	0.25	78.70	0.09
Tails	44.36	0.18	0.11	9.87	0.35
All collective concentrate	100.00	0.81	11.19	100.00	100.00

MAGNETIC SEPARATION

Magnetic separators have proved useful adjuncts to table and flotation concentration when tungsten ores contain cassiterite, pyrite, garnet and epidote. They are especially useful and indispensable for the separation of wolframite* and cassiterite, both of which are found almost universally together, in the Sino-Malayasian metallogenic province in particular.

There are two types of magnetic separators in common use, the Induction Roll type and the Wetherill type. As the principles underlying both types are familiar to all, any description of them is unnecessary. The Induction Roll type gives a more intensive field and a cleaner tailing; the Wetherill type, on the other hand, has a higher selectivity than the Industion Roll type. Both types of machine have their own province of usefulness and a judicious selection or combination of the two enables one to obtain the optimum results for the treatment of particular types of ore.

It should be emphasized that with concentrate finer than 180 mesh, the electromagnetic separation of wolframite from cassiterite can hardly be effected. If it is found that the wolframite concentrate contains considerable tin cemented by iron oxide, as happens sometimes, good separation can be effected only by the initial use of hot sulfuric acid to dissolve away the iron oxide cement.

Pyrite can be separated from tungsten concentrates by a magnetizing roast followed by magnetic separation. "The pyrite must be present in individual grains for complete separation; the more grains the more effec-

---

* It has been suggested by Dr. David Williams [*Trans. Inst. Min. Met. (London)*, **LII**, 182 (1943)] that wolframite coming from the inner, deeper, zones would be slightly more magnetic than that derived from localities further away from the granite, because since the Fe^{++} ion is smaller than the divalent manganese ion, the earlier wolframite should be richer in the $FeWO_4$ molecule than that which separated out later.

tive the separation by magnetic means. The thoroughness of the magnetizing roast is another factor. The object of roasting is to form a magnetic film that will adhere to the particle.

"The important factors in roasting are the size of the particles, the temperature and the time. Coarse particles require appreciably longer to heat to ignition temperature than fine ones. A temperature at least equal to the ignition temperature of pyrite must be maintained long enough for a film to form. The time of roasting need not be prolonged beyond this point. If the temperature is high enough the film will form in a few moments.

"The physical appearance of the roasted product is a guide to roaster operation. A good magnetizing roast is indicated by the absence of characteristic pyrite particles and by a flat, dead color ranging from bronze to black. Black is characteristic of a deficiency of air during roasting or of a reducing atmosphere. The color of the roasted product is affected by the amount and color of other minerals present, which may or may not be altered by roasting."

The results of the experiments by Glembotsky to apply magnetic separation to tin-tungsten concentrates indicate that with a field strength of 17,600 gauss and an amperage of 8 amperes, a 78-per cent extraction of WO_3 would be possible, and that if the concentrates were preliminarily heated at 600° for 5 minutes a Wetherill separator gave an extraction of 86 to 96 per cent of WO_3, with 85 to 92 per cent cassiterite remaining in the tailings.

In China large-scale operations of magnetic separation of tin-wolfram concentrate have given excellent results. With the Krupp type of magnetic separator, the following results have been obtained. A concentrate containing 13 per cent WO_3 and 50 per cent tin, after being crushed to pass through 16 mesh, yielded a tungsten concentrate containing 66 per cent WO_3 and 0.8 per cent tin, and a tin tailing containing 69 to 72 per cent tin and 1.5 to 2 per cent WO_3. If the average composition of twenty lots of tinny wolfram concentrate is assumed to be 68.3 per cent WO_3, 2.3 per cent Sn and 0.13 per cent As, the magnetic separator gave an average concentrate containing 72.1 per cent WO_3, 0.5 per cent Sn and 0.09 per cent As.

Garnet and epidote, the usual minerals present in contact-metamorphic deposits, can hardly be separated from the tungsten minerals by gravity methods without sacrificing recovery. As they are highly magnetic, they are taken off on cross-belts of the magnetic separators.

AIR-TABLING

Pneumatic methods of concentration for tungsten ores have been tried, but have been proved inadequate for satisfactory results. Aside from the necessity of careful grading of the sizes of the particles, the dust problem always proves troublesome. Recent improvement in the design of air tables, such as that of Sutton, Steele & Steele, may prove of value to the problem of dealing with low-grade tungsten concentrates.

ELECTROSTATIC SEPARATION

The theory of electrostatic separation is not new, but the practical application of this principle to industrial ore dressing is relatively recent. The electrostatic separator makes it possible to separate mineral particles of different electrical conductivities. As the minerals come off a feed pan onto a brass roll, which is grounded, they are charged by a needle electrode discharging at 20,000 volts. The good conductors lose their charge to the roll, while the poor conductors retain their charge. The good conductors then leave the roll under the normal influence of gravity, while the poor conductors adhere to the roll. Briefly, this is the principle of the electrostatic separator. In practice, however, there are many complicating factors. Many minerals are neither good nor poor conductors in any decided degree. Their electrical conductivities are rather close. Under such circumstances the amount of charge to be given the particles, the velocity of the brass roll, the rate of feed, the temperature of the feed, etc., have all to be investigated in order to strike the proper balance of variables.

Cassiterite can be separated from scheelite by the electrostatic separator. Cassiterite is a fairly good conductor of electricity, but scheelite is not.

The surface characteristics of the minerals have some influence on the efficiency of the operation. Any iron stain contaminating the scheelite mineral, due to whatever causes, may increase the electrical conductivity of the scheelite mineral; and pyrite, which is normally a good conductor, may be rendered a poor conductor if it has undergone surface oxidation.

FLOAT-AND-SINK PROCESS

The float-and-sink process has been applied to coal beneficiation for a long time but its application to ore concentration is of only recent date. Its field of usefulness may be extended in the future to the beneficiation of tungsten ores.

If the tungsten minerals can be freed from the associated gangue minerals at a reasonably coarse size, the float-and-sink process may be applied for this concentration. The ore fed to the separating unit of this process should be as clean and dry as is practically possible, and should be washed free of slimes and sand to prevent a rise in the viscosity of the medium used. The range of sizes in the feed can be much wider than the range treated on jigs. The condition of the mineral aggregation will determine the upper size, and the viscosity and density of the medium will determine the lower size limit—generally about 8 mesh. The so-called "M.B.I. Process" (patented sink-and-float process) of the American Cyanamid Company may treat sizes as fine as 35 to 48 mesh, according to information given.

The suspension media that have been tried in the float-and-sink process as applied to concentrating tungsten ores are galena and ferrosilicon. The mineral galena having a specific gravity of 7.5 can be used to make suspensions with a maximum gravity of 4.3. The specific gravity of the ferro alloys containing 10, 15 and 25 per cent silicon is, respectively 7.0, 6.8 and 6.3; and suspensions having a maximum gravity of about 3.5 can be made from a 15-per cent ferrosilicon. The reclamation of the medium used forms an important part in this process. The loss of medium per ton of ore treated is always insignificant.

The sink-and-float pilot plant at Barking, England, has experimented with galena as suspension medium for the beneficiation of tungsten ores. It has been reported that the Pan-American Tungsten Corporation has installed a sink-and-float mill in the Isle of Pines, Cuba, for the treatment of tungsten ores, using ferrosilicon as the medium.

ACCESSORY PROCESSES

(1) **The Murex Process.** The Murex Process may be adopted as an adjunct to a tungsten milling plant to remove sulfide minerals, especially such minerals as pyrite and arsenopyrite, if present in an appreciable amount, from the tungsten concentrates. The Mawchi Mine in Burma has adopted such a process to treat the concentrates from the jigs assaying about 32 per cent Sn, 25 per cent WO_3, and 8 per cent combined arsenic and sulfur. "After drying on a hot-plate the concentrates are elevated to a bin and thence fed to a 4-mm. Newago screen. Oversize is crushed, since the magnet cannot effectively deal with particles over 4-mm. Undersize is screened on a 60-mesh screen to remove fines which must be treated by flotation."

Magnetite and fuel oil in the ratio of 3:1 by weight are fed into a mixer 3 ft high x 3 ft diameter which has revolving paddles. When thoroughly mixed, the product is fed by a hand-pump into a service tank where agitation is continued to prevent settlement. The sized concentrate with 5–6 per cent by weight of the magnetite oil paint is fed continuously into an agitator together with an equal weight of water to which sufficient sulfuric-acid has been added to maintain the pH value at 2.8. Coarse sulfides are carried in the agitator to prevent binding of the mix and to assist in coating sulfides, their exit being stopped by a screen at the discharge end. The feed is 1.1 tons of concentrate per hour. The agitator is 9 ft long, 3 ft 6 in in diameter and revolves at 25 rpm.

"During agitation the sulfide particles become coated with the magnetic paint which will not adhere to the cassiterite and wolfram in acid circuit. The mix discharged onto a shaking tray which carries it under a magnet, the coated sulfide particles being removed thereby and thrown to one side by a cross belt. The cassiterite and wolfram are classified, settled, dried on a plate and are then ready for bagging. The assay is about 28 per cent Sn, 32.5 per cent WO_3, 0.6 per cent As, and 0.6 per cent S.

"The paint-coated sulfides are treated in a furnace to drive off the oil; then the magnetite is recovered magnetically, the sulfides being rejected. The temperature maintained in the furnace is high enough to burn off the oil without roasting the sulfides, but a certain amount of arsenic is unavoidably volatilized and is caught in condensing chambers."

(2) **The leaching process** may be adopted to treat tungsten concentrates containing an appreciable amount of apatite. According to J. B. Clemmer and R. G. O'Meara, "the amount of acid required for leaching depends on the grade of the concentrates and associated gangue. A small amount of acid is sufficient when the gangue is siliceous. Concentrates assaying 73.32 per cent WO_3 and 0.295 per cent phosphorus, treated with 12 pounds of commercial hydrochloric acid per ton of concentrates, gave a residue assaying 0.007 per cent phosphorus and 75.24 per cent WO_3. The loss of tungsten was negligible. No attempt was made to determine the acid consumption.

"Concentrates from the contact metamorphic ores contain calcite and require more acid. A ton of 50-per cent WO_3 concentrates theoretically required a ton of commercial hydrochloric acid (18° Bé) to dissolve the calcite. An excess is necessary to ensure complete solution of the apatite. A concentrate assaying 48.54 per cent WO_3 and 0.266 per cent phosphorus was leached with a slight excess of acid. The residue assayed 77.96 per cent WO_3 and 0.009 per cent phosphorus. The loss of tungsten was small. The tungsten dissolved probably reprecipitated at the moderate acid concentration due to the abundance of calcium salts in the leach liquor.

"As leaching is so effective it might be used to remove the apatite rather than to depress it in flotation and incur an unavoidable loss of tungsten. The increased tungsten recovery would partly offset the added expense of leaching. The flotation would be more flexible and require less technical skill and supervision."

(3) **The roasting process** may be adapted for the elimination of arsenic from tungsten ores or concentrates containing a high percentage of arsenic. According to J. H. Brennan [U. S. Pat. 1,790,088 (Jan. 27, 1931)] arsenic can be substantially removed from the ore or concentrate when the ore or concentrate, ground to 10 mesh or finer, is subjected to roasting to 800°

in conjunction with elemental sulfur. As an example, wolframite, containing 1.76 per cent arsenic, was ground to 40 mesh, mixed with 5 percent its weight of elemental sulfur and heated to 800° for three hours. After this treatment the ore contained only 0.03 per cent arsenic.

Representative Tungsten Milling Plants

As illustrations of the methods of concentrating tungsten ores several typical tungsten milling plants are described. They are taken *in extenso* from articles appearing in different journals and technical publications.

(1) **Mining and Milling Tin-Tungsten Ore at Mawchi Mine, Burma.*** The valuable minerals contained in the ore are cassiterite, wolfram, and scheelite. Non-valuable metallic minerals are sulfides, notably pyrite, arsenopyrite, chalcopyrite, and galena, all in small quantities. The gangue consists of quartz, granite, and killas.

The principle adopted in milling this ore is a carefully controlled reduction in particle size with removal of values as soon as released from the matrix. To this end all middlings are screened and recirculated, sometimes after grinding. Tailings from the main mill pass to the tailings plant where they are sized and tabled, the coarser part having been re-ground.

The mill is designed to produce a concentrate of 70 per cent tin and tungstic oxide (WO_3) with a minimum of sulfides and a maximum particle size. This latter is of great importance, not only because the maintenance of particle size improves recovery, but also because with concentrate finer than 180-mesh, the electromagnetic separation of wolfram from cassiteriter cannot be effected and the less satisfactory chemical method entailing the conversion of wolfram into sodium tungstate must be used.

All concentrates are re-treated with the object of reducing the arsenic and sulfur contents to less than 1 per cent. The fines are cleaned by batch flotation and the coarse by the Murex process in which the sulfide particles are coated with a paint of oil and magnetite and removed magnetically.

About 12,500 tons of ore can now be treated monthly, the run of mine ore having a head assay of about 2.5 per cent mixed tin and tungstic oxide in approximately equal parts and a moisture content of 8 per cent. The recovery is about 90 per cent for tin and 83 per cent for wolfram.

Two apron feeders transfer the ore from the bin onto a 24-in conveyor belt which discharges on to a swinging grizzly with 2½-in apertures. Oversize passes into a 14 x 10-in Blake crusher set at 2½ inches. Undersize and crushed product pass into a 15-mm trommel. Oversize goes to a 35-ft x 24 in picking belt moving at 50 rpm, over which is suspended an electro-

---

* J. E. Denyer and K. C. G. Heath, *Trans. Inst. Min. Met., London* (1940).

recoverable values, though it may be apparently barren. The waste picked amounts to about 3.5 per cent of the feed and is of lower assay value than the final tails.

The picking belt feeds a 5-in Newhouse crusher, and discharge from this and from the trommel go to a series of Leahy screens with 30 x 14-in rolls grinding in closed circuit. The material produced is of the following sizes: −8 + 6 mm, −6 + 3 mm, −3 + 1.4 mm, and −1.4 mm. The first three go to the jigs and the last is classified, the underflow going to the jigs and the overflow to tables. Sectionalized flow sheets will be found in the figures on pages 135 and 137.

The jigs, with the exception of Nos. C1 and C2, are of the Hartz type and jigging is through the screen (following table). Ragging is concentrate slightly larger than the mesh size. Screens are raked about every 15 minutes to stop blinding. Jigs C1 and C2 are of the Bendelari type (see figure). In this jig the pulsations are produced by the movement of a circular metal plunger placed horizontally under the jig screen and connected to the body of the hutch by an annular rubber diaphragm. A stream of water is added below the screen, the opening being controlled by a flap valve which closes or tends to close on the up stroke, thus reducing excessive suction through the jig bed on the down stroke. Concentrate falls into pockets on either side of the diaphragm and is drawn off through spigots.

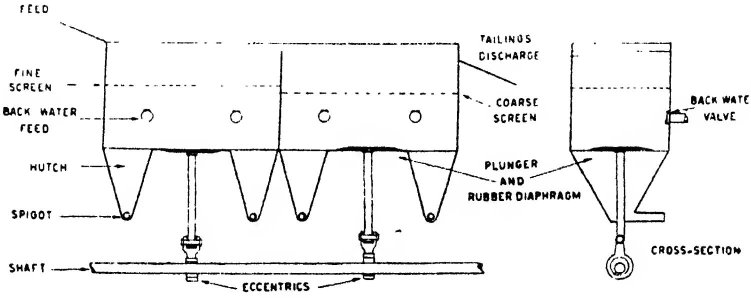
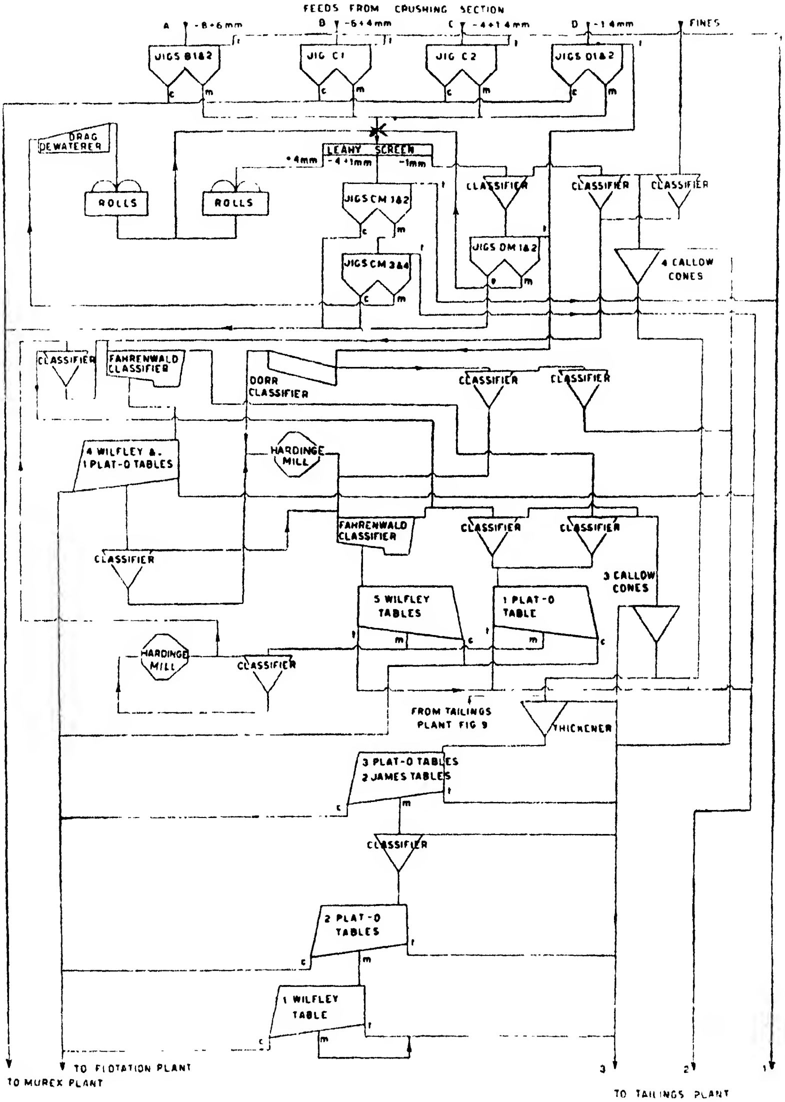


Diagram showing the principle of a two-compartment Bendelari jig.

Details of Jigs

Name	Number	Type	Screen area (sq.ft)	Hutches	Size of feed (mm)	Screen (mm)	Pulsations per min
B	2	Hartz	20.5	4	−8 + 6	10	200
C1	1	Bendelari	49.0	4	−6 + 4	8½	180
C2	1	"	36.75	3	−4 + 1.4	6½	140
D	2	Hartz	15.0	4	−1.4	3	360
CM	4	"	20.5	4	−4 + 1	6½	180
DM	2	"	12.0	3	−1	2 & 3	360

There are four primary jigs all making a concentrate for the Murex plant, and a middling for the middling jigs; but whereas the tailing from the three coarser jigs goes to the tailings plant, that from the finest jig goes to the tabling section.



Flowsheet of jigging and tabling section.

There are three pairs of middling jigs. The first pair has a feed of −4 magnet to remove tramp iron. Ten women pick out killas, wood chips, etc., from the ore on the belt. No granite is removed as it often contains + 1 mm and sends concentrates to the Murex plant, tails to tailings plant, and middlings to the second pair of jigs for retreatment. The third pair of jigs takes the −1 mm middlings from the primary jigs, fines having been removed and sent to the tabling section. Again, concentrates go to the Murex plant while tailings go to the main tabling section. All middlings from the second and third pairs of jigs are close-circuited through fine rolls.

All slimes classified out of the jigging circuits are dewatered in Callow cones, the underflow going to the slime tables in the main mill and the overflow to the thickener in the tailings plant.

The main tabling section consists of Hardinge mills working in conjunction with Fahrenwald classifiers feeding Wilfley and Plat-O tables. Middlings are close-circuited through the Hardinge mills.

Slimes produced in the tabling section are dewatered in Callow cones and join the products from the cones which deal with jig fines. These slimes are fed via a spitzkasten to Plat-O and James slime tables from which a concentrate is taken to the flotation plant. The middlings are classified and treated on Plat-O tables, from which middlings go to a Wilfley table. Both middlings and tails from this table go to the tailings plant as do the tails from all other tables in this section. All concentrates go to the flotation plant.

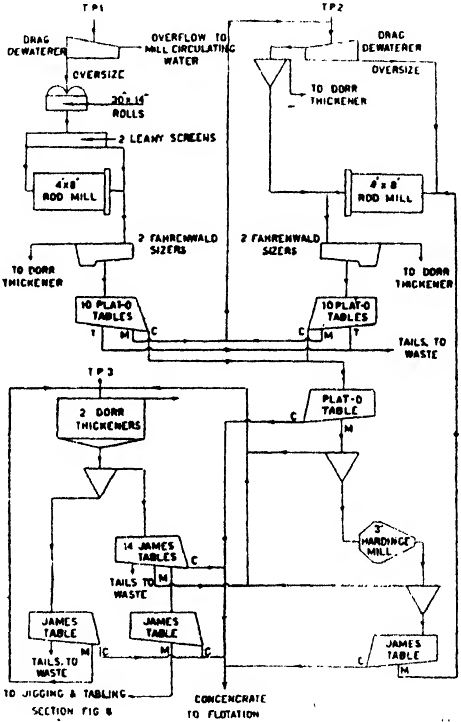
Feed to the tailings plant is in three parts. In the upper section the coarse tailings received from the jigs are ground by rolls and rod mills to −1 mm and fed to two Fahrenwald classifiers, the ten spigots of which feed ten Plat-O tables. The concentrate is sent to the retreatment table for final cleaning before going to the flotation plant. Middlings go to the second section of the tailings plant and the tailings to waste, the tin and wolfram content being too small to justify further crushing.

The second section deals with the middlings from the first section and the feed from the main mill as mentioned above. After dewatering, the pulp is ground in a rod mill further to release values, and distributed to ten Plat-O tables by two Fahrenwald classifiers. Heads go to the retreatment table, middlings are close-circuited through the rod mill, and tailings go to waste.

Middlings from the retreatment table are classified, and after grinding in a 3-ft Hardinge mill are passed onto a James table which gives two products: a head fit for flotation and a tailing which is returned to the rod mill.

In the third section of the tailings plant, which deals with the finest tailings from the main mill together with any slimes made in grinding in the tailings plant, the feed is dewatered in a Dorr thickener and sent to fifteen James slime tables, which yield a clean concentrate, a first middling which is retreated on one James slime table, a second middling which is returned to the thickener, and a tailing which goes to waste.

About 8 per cent of the total concentrate recovered comes from the tailings plant.



Flowsheet of tailings plant.

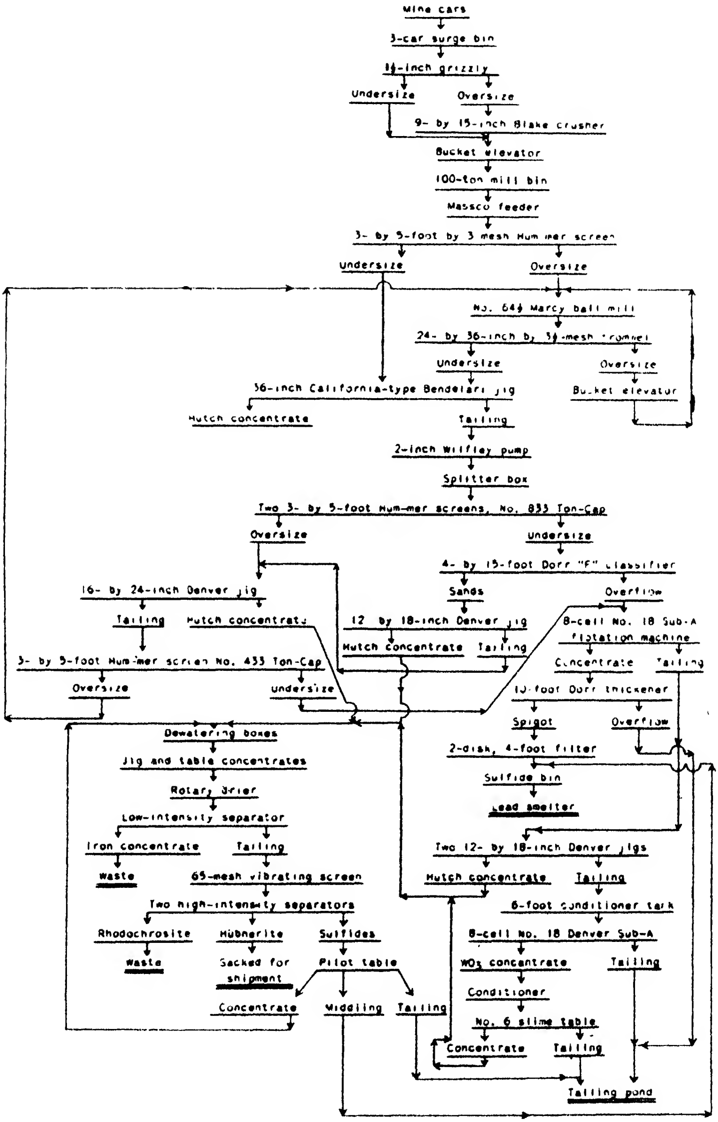
Concentrates from the jigs, assaying about 32 per cent Sn, 25 per cent WO_3, and 8 per cent combined arsenic and sulfur, are taken to the Murex plant for the removal of sulfides. Description of the Murex and flotation plants has already been given.

(2) **The Ima Mill of the Ima Mine, Blue Wing District, Lemhi County, Idaho.*** The ores handled in this mill vary widely in metal content, gangue constituents, and physical characteristics. The gangue of the ore

---

* Dice, C. M., "Methods and Costs of Concentrating Hübnerite ores at the Ima Tungsten Mine, Lemhi County, Idaho," Inf. Cir. 7230, U. S. Bureau of Mines, (Jan. 1943).

received at the mill is predominantly quartz, with varying amounts of fluorite, rhodochrosite, mica, talc and pyrite. The ore minerals are hübnerite, silver-bearing tetrahedrite, galena, chalcopyrite, sphalerite and molybdenite.



Flow chart of Ina Mill. *From C. M. Dice, U. S. Bureau of Mines.*

A typical analysis of the mill head is as follows:

Au	Trace
Ag	1.85%
Cu	0.2%
Pb	0.25%
Fe	2.6%
Insoluble	88.2
Zn	0.2%
S	2.1
WO_3	0.52%
MoS_2	0.1%

Crushing. Ore is received at the mill in trains of six to eight mine cars, each of 16 cu ft capacity. No primary storage is provided, and the cars are dumped directly onto an 8-in horizontal rail grizzly which covers a small surge bin of two to three car capacity. Oversize lumps are hand-sledged through the grizzly.

The ore is fed by hand to a 9 x 15-in Blake-type jaw crusher set to 1½ inches. The ore shatters readily, and the crusher has a capacity of 225 cars per 24 hours. The crusher discharge joins the grizzly undersize and is delivered to a 100-ton mill bin by means of a bucket elevator which is driven from the extended crusher shaft.

Grinding and Classification. An adjustable stroke feeder delivers the ore from the mill bin to a 3 x 5-ft x 3½-mesh vibrating screen. The oversize is fed to the ball mill, and the undersize is laundered to a 36-inch single-cell Bendelari jig, which also receives the ball-mill discharge. The ball mill discharges through a 24 x 36-in spiral screen equipped with a 3 x 3-mesh steel cloth. Screen oversize is elevated and returned to the ball mill; the undersize joins the primary screen undersize at the Bendelari jig.

The grinding unit consists of a No. 64½ Marcy ball mill equipped with ⅜ x ½-in compensating grates and operates in closed circuit with vibrating screens and a 15 x 4-ft Dorr "F" classifier. At the present time the mill receives about 120 tons of ore per day from the storage bin. The return to the ball mill, consisting of spiral screen oversize, vibrating screen oversize, and screened classifier sands amounts to approximately 200 tons per day. The mill operates at a speed of 26 rpm and is driven from the main mill line shaft, which is V-belt connected with the ball-mill pinion shaft from a No. 20 Lemley clutch.

The ball mill is operated with a comparatively low pulp density that ranges from 55 to 60 per cent solids. Manganese steel breast liners, end liners, and grates are used. A relatively light ball-load is maintained, averaging 600 to 700 pounds. Ball wear is compensated by the addition of 4-in hardened forged steel balls. Under these operating conditions, the steel consumption is relatively high, being approximately as follows per ton of initial feed:

	Pounds
4″ forged steel balls	2.25
Breast liners	0.40
End liners	0.05
Grates	0.03

Chilled cast balls have been used. However, breakage was high and the accumulation of ball iron on the jigs, with the resulting blinding of the beds, made their use uneconomical. Ball consumption, when using this type, was between 6 and 7 pounds per ton of ore.

Screen classification is used in order to immunize the over-grinding of heavy mineral particles of finished size which inevitably occurs in the use of hydraulic classifiers alone. The classification flow sheet, which may appear to be unduly complex, was designed first to eliminate as far as possible overgrinding the tungsten minerals, and secondly to deliver prepared feeds to the jigs, rather than for the simple removal of finished sands.

The Bendelari jig tailings are pumped to the top floor of the mill building, and discharged into a splitter box which divides the feed between the two secondary screens. Two 3 x 5-ft Hummer screens equipped with No. 833 ton-cap stainless steel cloth having openings 0.074 in wide (14-mesh), are used as this point. Undersize from the screens discharges into a 15 x 4-ft Dorr "F" classifier, while the oversize is laundered to a 16 x 24-in two-compartment Denver jig. The classifier, which operates principally to deslime the fine jig sands, is set on a slope of three inches per foot and operates at a speed of 28 rpm. Classifier overflow at about 15 per cent solids is laundered to the first cell of the sulfide flotation unit. Classifier sands are passed over a 12 x 18-in two-compartment Denver jig and then join the oversize from the secondary screen at the large Denver jig. Tailings from this jig are screened on a 3 x 5-ft Hummer equipped with No. 433 ton-cap stainless steel cloth having an opening 0.021 in wide (30-mesh). Screen oversize returns to the ball mill. Screen undersize is pumped to the third cell of the sulfide flotation machine. Screen efficiencies vary from over 90 per cent with a new screen cloth to about 75 per cent just before replacement of the cloth.

Jigging. The major recovery of tungsten from the ore is obtained on the primary jigs included in the grinding circuit. The ball mill discharge, after removal of the plus 3-mesh material is treated on a 36-in California type Bendalari jig. The jig is operated at 150 rpm, using a $\frac{5}{8}$-in stroke. Most of the plus 20-mesh hübnerite as well as a considerable portion of the plus 200-mesh material is recovered at this point. Pyrite is largely rejected and the concentrate averages between 36 and 40 per cent WO_3. Tailings from this jig are screened on 20-mesh and the undersize deslimed before further jigging. The classifier here serves the double purpose of removal of excess water and minus 150-mesh gangue, while allowing fine tungsten to concentrate in the sands. The sands are then jigged on a small two-compartment Denver jig operating at 300 rpm with a $\frac{3}{16}$ to $\frac{1}{8}$-in stroke. Tailing from this jig is used to dilute the plus 20-mesh sands for jigging on the 16 x 24-in Denver jig. A speed of 200 rpm with a $\frac{1}{4}$-in stroke is used on this unit. The concentrate produced consists mainly of coarse pyrite, assaying 12 to 20 per cent WO_3. Minus 40-mesh sands are then removed by screening before returning the sands to the mill for further grinding. Two small secondary jigs treat the tailings from the sulfide flotation machine, and account for approximately 15 per cent of the total jig recovery. Overall jig recovery amounts to approximately 65 per cent of the head content. All primary jig concentrates are combined at the dewatering box, producing a concentrate varying from 20 to 30 per cent WO_3 which is concentrated to shipping grade by magnetic separation.

Flotation. Classifier overflow and screen undersize at a pulp density of approximately 20 per cent solids is subjected to a bulk sulfide flotation step for the removal of a silver concentrate consisting principally of pyrite. The sulfide unit consists of an eight-cell No. 18 Denver Sub-A machine. The original blank of four cells is belt-driven from the line shaft. Two additional motor-driven units of two cells each have since been added. The first two cells produce a finished concentrate, and the remaining six cells produce a rougher concentrate which is returned to the first cell by gravity. Reagents used in this section (0.15 lb/ton isopropyl xanthate; 0.10 lb/ton pine oil) are added to the classifier overflow feeding into the first cell of the machine.

The sulfide concentrate produced after thickening and filtering is combined with the sulfide tailings from the magnetic separators and shipped to a lead smelter. The combined product assays as follows:

Au	Ag	Cu	Pb	Insol.	Fe	Zn	S
0.01	45.0	3.8	7.0	9.0	29.2	4.8	37.6

Tailings from the sulfide unit are split to two 12 x 18-in Denver jigs. Reagent for the flotation of slimed tungsten is added to the tailings from these jigs which discharge into a six-foot conditioning tank at 15 per cent solids. The reagent is made up of an emulsion containing 0.25 lb/ton oleic acid, 0.30 lb/ton Reagent No. 708, 0.05 lb/ton Emulsol X-1. Cost of this reagent averages 4.2 cents per ton of ore.

A second eight-cell No. 18 Denver Sub-A machine is used for the flotation of tungsten. The froth removed from this unit assays 4 to 6 per cent WO_3, most of the balance being made up of fluorite, sericite and rhodochrosite. Tailing from the flotation unit carries only traces of tungsten and is sent to waste. The concentrate is conditioned with sulfuric acid (0.5 lb/ton of ore), in order to break down the froth, and then is tabled for the rejection of fluorite and rhodochrosite. The flotation concentrate is thus graded up to 25 or 30 per cent WO_3 with a recovery of 50 to 55 per cent. A No. 6 Deister-Overstrom diagonal-deck slime table equipped with rubber deck and riffles is used. Table tailings carrying 1 to 2 per cent WO_3 join the flotation tailings and are laundered to the ponds. Assay of the combined tailings shows 0.07 to 0.10 per cent WO_3 and 0.2 to 0.25 ounce silver per ton. Elutriation tests show most of the tungsten content of the tailing to be in the minus 400-mesh fraction, and over 50 per cent in the minus 300-mesh portion.

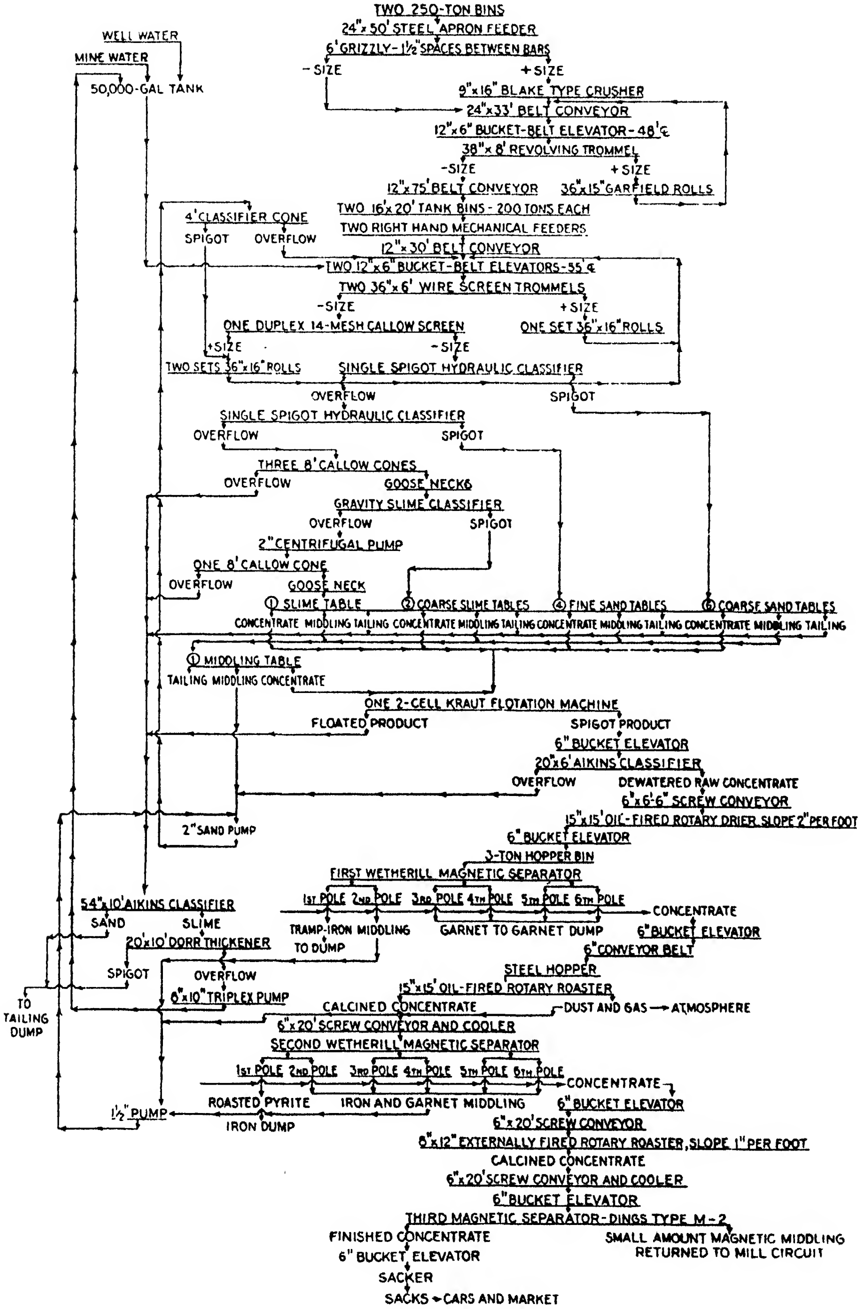
Magnetic separation of the flotation concentrate instead of the tabling operation is not feasible because of the large amount of rhodochrosite present, which has approximately the same magnetic susceptibility as hübnerite.

Magnetic Separation. The various jig and table concentrates produced are accumulated in dewatering boxes and dried at the end of the day in a small rotary tube furnace. The furnace consists of a sheet-iron cylinder 18 in in diameter and 15 ft lóng, set at a slope of two inches per foot. Material to be dried is fed by means of a scoop feeder and is discharged onto a concrete floor from which it is shoveled to storage bins. After cooling for 24 hours the dried concentrate is treated on the magnetic separators.

Dust from the drying furnace is caught in a baffled settling chamber and periodically treated at the separators. Six to eight hundred pounds per month of high-grade tungsten dust is recovered from this source.

Three magnetic separators are used in the final cleaning of the jig and table concentrates. One low-intensity machine serves to remove circuit iron plus any partially roasted pyrite which may have been formed in the drying operation. A small vibrating screen is attached to the discharge of this machine, and removes the minus 60 mesh material for separate treatment. Two Dings type E, two-pole separators treat the screened portions of the concentrates for the removal of finished tungsten concentrate. The first machine, with a belt width of 12 in, draws 16 to 18 amps, while the second with a belt width of 24 in draws 32 to 38 amps.

The pole gaps are adjusted to conform to the size of the material being treated and to the impurities present. For those concentrates which carry considerable rhodochrosite and siderite, the gap on the first pole is widened and these impurities are removed ahead of the tungsten. The feed rate is governed by the appearance of the streak on the table to which all separator tailings are fed. In general, a feed rate of approximately 250 pounds per hour per foot of belt width is used on the plus 65-mesh feed; rates somewhat less than half of this are required for the minus 65-mesh portions. A small cut is removed from the pilot table and returned to the separators, accounting for approximately one per cent of the total production.



Flow chart of tungsten concentrates at Mill City, Nevada.

The overall recovery at the separator units varies from 95 to 97 per cent, practically complete recovery being obtained on the plus 100-mesh feeds. Final concentrate is sacked in paper-lined canvas bags holding 100 pounds each.

(3) **Concentration of Tungsten Ore by the Nevada-Massachusetts Company.***

"The following may be considered a typical analysis of the mill feed (specific gravity 3.1):

	Per Cent		Per Cent		Per Cent
WO_3	1.24	S	1.44	As_2O_3	Trace
SiO_2	47.06	P	0.24	SnO_2	Trace
Fe_2O_3	10.89	MgO	0.48	CO_2	5.34
Al_2O_3	8.76	CuO	0.06	ZnO	0.08
MnO	1.01	MoO_3	0.05	NiO_2	0.02
CaO	23.52	Bi_2O_3	0.03		

"Two parallel bins of 250 tons each receive the ore. Eight R & P. gates, 24 by 30 in, control the discharge from the two bins on a variable-speed, clutch-controlled, steel apron conveyor between the two bins, which discharges to a grizzly. A Blake-type crusher reduces the oversize, which joins the grizzly undersize on a belt conveyor discharging into a 14-in by 48-ft belt-and-bucket elevator, equipped with 12 x 6-in buckets spaced 16 in apart. The conveyor speed is 280 ft per minute and the elevator speed is 300 ft per minute. This elevator discharges into a revolving trommel, $\frac{3}{16}$-in steel plate, $\frac{9}{16}$-in holes, 20° slope and 19 rpm. The trommel oversize drops into a set of Garfield rolls, set to $\frac{1}{2}$ in, 63 rpm, operating in closed circuit with the conveyor, elevator and trommel.

"A set of rolled chrome-steel shells on this work reduces 56,000 tons of ore, showing a steel consumption of 0.034 lb per ton.

"The trommel undersize passes to a belt conveyor equipped with a hand-propelled tripper, which discharges into two cylindrical redwood-stave tank bins.

"A right-hand mechanical feeder attached to the bottom of each of these tanks feeds onto a conveyor, speed 300 ft per minute, which delivers the ore to two 14-in by 55-ft belt-and-bucket wet elevators, speed 300 ft. per minute, which discharge into one of two trommels equipped with No. 23 Ton-Cap screen, $\frac{1}{8}$ by $\frac{1}{4}$-in openings. The percentage of openings is 38.

"The trommel oversize passes to a set of rolls, 95 rpm, operating in closed circuit with the wet elevators and trommel. The set of these rolls is varied with the amount of the circulating load. If the load is seen to be building up, the rolls are set up a little closer. The undersize passes to a

---

* Otto F. Heizer, *Trans. Am. Inst. Min. & Met. Engineers*, Vol. **112**, pp. 833–840 (1934).

duplex Callow screen equipped with 14-mesh phosphor-bronze Ton-Cap screen. Two sets of rolls receive the Callow-screen oversize, grinding in closed circuit with the elevators, trommel and Callow screen.

"Cast-steel roll shells grinding the trommel oversize last approximately five months and show a steel consumption of 0.063 lb per ton. Cast-steel shells on the rolls grinding the Callow-screen oversize and table middling last approximately seven months and show a steel consumption of 0.045 lb per ton.

"The 14-mesh Callow-screen undersize flows to a single-spigot hydraulic classifier, which delivers coarse sands through a spigot to six Wilfley and Deister-Overstrom tables. The overflow goes to a second single-spigot hydraulic classifier, which delivers fine sand through the spigot to five Wilfley and Deister-Overstrom tables and overflow which goes to three 8-ft Callow cones. The Callow-cone goosenecks discharge into a simple nonhydraulic classifier, which roughly separates the coarser and heavier from finer and lighter products. The coarser and heavier part of the slime passes through a spigot and is dressed on two Wilfley tables. The finer and lighter part flows to a centrifugal pump, which delivers it to a single Callow cone. The gooseneck product from this cone is dressed on a Deister table. All Callow-cone overflows go into the tailing launder.

"All tables produce a concentrate, middling and tailing. All table middlings flow to a single Deister-Overstrom table for redressing. A broad middling flows from this table to a centrifugal pump, which delivers it to a cone above the fine rolls. The spigot from this cone drops into the fine rolls grinding the Callow-screen oversize and the cone overflow joins the feed and circulating load in the wet elevators.

"The raw concentrate flows to a two-cell Kraut flotation machine, which eliminates the fine sulfide minerals. The flotation tailing, consisting of the scheelite together with coarse pyrite and garnet, flows into a bucket elevator discharging into a small Akins classifier, for dewatering. The overflow from the classifier joins the table middling and goes back into the mill circuit. The raw concentrate, averaging 50 per cent scheelite, now reduced to 7 per cent water drops into a screw conveyor, and is delivered into the upper end of an oil-fired rotary drier running at 10 rpm, designed and built on the property. Oil consumption is estimated at one gallon per hour. The dried concentrate drops into the boot of a belt-and-bucket elevator, which discharges into a hopper bin. The operation up to this point is continuous throughout the three shifts. The roasting and magnetic separation is confined to two shifts.

"The dried concentrate that has accumulated in the hopper bin is fed evenly onto the belt of the first magnetic separator. Continuous current is supplied by a motor-generator set consisting of a 10-hp, 11-40-rpm, 440-

volt, alternating-current motor belted to a 6-kw, 125-volt, 48-amp, 1180-rpm generator. Magnetic characteristics of the first magnetic separator are as follows:

Poles	Ampere Turns	Amperes	Volts
2	30,000	1.4	120
2	60,000	11.4	120
2	100,000	21.4	120

"Tramp iron is removed by the first pole and goes to the dump, a small quantity of pyrite granules that have been reduced in drying is removed by the second and third poles and delivered to the middling pump and returned to the mill circuit. The fourth, fifth and sixth poles remove the bulk of the garnet, which is wheeled to a separate garnet dump.

"The discharged raw concentrate from the first Wetherill magnetic separator passes into a belt-and-bucket elevator and from there to a belt conveyor and into a steel hopper at the feed end of the rotary oil-fired roaster. This roaster consists of a tube 15 in in diameter by 15 ft long, lined with firebrick and tile, slopes 2 in to the foot, rotates at 10 rpm and consumes an estimated 1½ gal of 27° Bé oil hourly. Time of contact in the roaster is approximately five minutes. The temperature carried is sufficient to ignite the sulfur only. The aim is to produce a magnetic sulfide on the surface of the pyrite grains. If the roast is carried too far, only faintly magnetic Fe_2O_3 results. It has not proved feasible to dry and roast in one operation on account of the low fusibility of some of the garnets, which results in a tendency to clinker. Dust and gases are collected from the roaster stack and hot calcined discharge by a 36-in motor-driven exhauster and delivered to a 30-in by 8-ft cyclone dust precipitator. Collected dust, sweepings, middlings, etc., are pumped to the middling pump, which returns these products to the mill circuit.

"The hot calcined concentrate is discharged into a steel screw conveyor, where it is spray-quenched with a small amount of water and cools in transit to the second Wetherill magnetic separator. This machine is similar to No. 1 magnetic separator and is equipped with a similar direct-current motor-generator set. The magnet characteristics are as follows:

Poles	Ampere Turns	Amperes	Volts
2	30,000	3.5	.120
2	60,000	11.4	120
2	100,000	21.4	120

"The first pole removes the reduced iron sulfide, which is wheeled to a separate iron dump. The second, third, fourth, fifth and sixth poles remove a middling product composed of both iron and garnet, with attached scheelite, which goes back into the mill circuit. The concentrate goes into a belt-and-bucket elevator and from there to a steel screw conveyor, which delivers it to an externally oil-fired rotating tube, at 6 rpm, where it is dead-roasted to eliminate residual sulfur and carbon. Estimated oil consumption is 1½ gal hourly. The calcined concentrate is discharged into a steel screw conveyor where it cools in transit to a belt separator, type M-2, which removes a very minute quantity of magnetic material. The finished concentrate is elevated by a belt-and-bucket elevator to a hopper, from which it flows through a 1¼-in pipe into a sacker.

"The finished concentrate is double-sacked, canvas inside of burlap. The sacks empty are 14 by 24 in, holding, when full, approximately 0.55 cu ft of concentrate and weighing 120 lb. The average car shipment is 70,000 lb of concentrate.

"Mill tailings flow through a launder to an outside building. A 54-in x 10-ft Akins classifier divides it into sand and slime products in the ratio of 75 and 25. The slime flows into a 20 x 10-ft Dorr thickener, which produces a clear over-flow and a spigot product averaging 3.7 :1 density. This spigot product joins the classfier sands and carries the tailing down the dump with an average pulp density of 1.15:1. The Dorr overflow is pumped up to a 50,000-gal tank above the mill, where it joins water pumped from the mines and such additional water as may be required from the valley well."

(4) **Milling Tungsten Ores at Pine Creek.***

"The process which has been developed by the United States Vanadium Corporation to treat the complex Pine Creek tungsten ores is unique in that straight flotation treatment is adopted and that the resulting low-grade tungsten concentrate is treated with steam and sodium carbonate in a digester under a pressure, followed by acid treatment, to give a final product of tungsten oxide. (See diagram, p. 148).

"The ore bodies are large masses of garnet along or near a contact of lime and granite, and contain scheelite, molybdenite, chalcopyrite and chalcocite with silver, molybdite and powellite, apatite, fluorite and various oxidized copper minerals, together with a small content in gold.

"The ore is conveyed to a 20-in gyratory crusher, crushing to 4 in at 160 tons per hour. The crushed ore is then fed over a ½-in screen to a Symons 5½-ft short-head crusher set at ¼-in opening.

"From the storage bins the ore is fed to four-open-end Marcy ball mills, 6 ft in inside diameter and 5 ft long, in closed circuit with 60-in Akins classifiers set to deliver a minus 60-mesh product, which is sampled by an automatic sampler at each machine.

"The mill is arranged in four separate sections. In each section, from the classifier, the ore pulp at a pulp density of 25 per cent solids flows by gravity to 10-cell 18-in impeller, M. S. type Stearns-Roger flotation ma-

---

* Blair Burwell, *Min. Cong. J.*, p. 16–18, (1941).

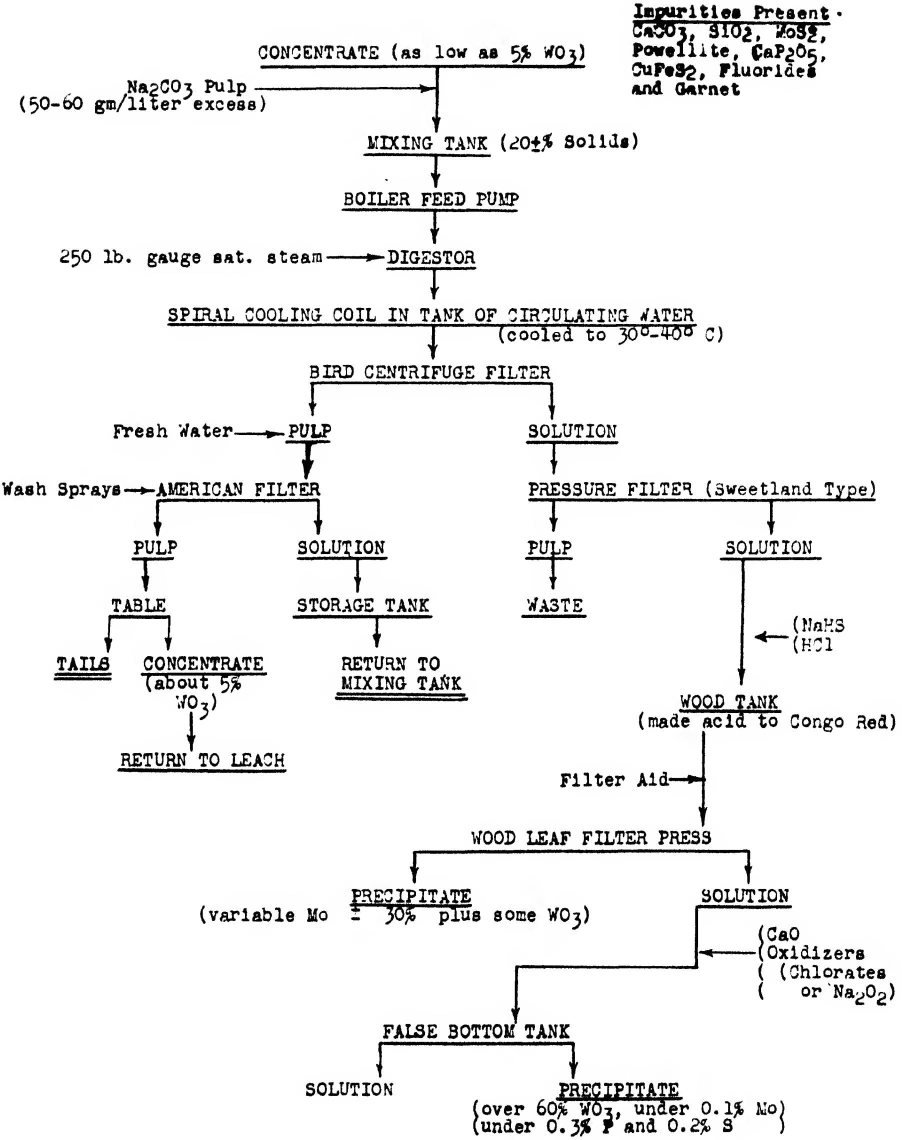


Diagram showing treatment of tungsten ores at Pine Creek.

chines. At this point sodium silicate, pine oil and xanthate are added without conditioning, to the pulp, and a bulk concentrate, containing approximately 20 per cent MoS_2, 20 per cent Cu and 30 oz of silver, is removed. This bulk concentrate goes to a cleaner circuit where the reagents are removed with steam, molybdenite is floated, and the copper-silver depressed with cyanide. A final molybdenite concentrate is produced from this circuit, and the copper-silver tailings from cleaner cells is shipped to the smelter as a copper concentrate. The final molybdenite concentrate contains approximately 90 per cent MoS_2 and 0.40 per cent copper, and the copper concentrate 29 per cent Cu, 45 oz of silver and $2.50 in gold.

"Following the sulfide flotation, the pulp is divided into two banks of cells of 10 cells each, of the same size, as are used in the rougher sulfide flotation. Cresylic acid, Emulsol and sodium oleate are added at the junction box of the cells for the flotation of scheelite.

"The unclassified pulp from each section of cells after flotation goes to two Deister tables, which serve as pilot tables to show unfloated scheelite, and pass from the tables to the tailings launder of the mill, which is equipped with an automatic sampler. The flotation concentrate is pumped to a thickener and is fed to pressure vessels by special high-pressure pumps and a specially designed mechanical arrangement, at a rate of approximately 40 tons of concentrates per day per vessel. The digested concentrates are filtered on a cascade series of three American-type leaf fillers with repulpers between each filter. The filters are equipped with steam blow connections to prevent blinding of filter cloths. The chemically treated concentrates join the ore tailings over a pilot table for telltale purposes.

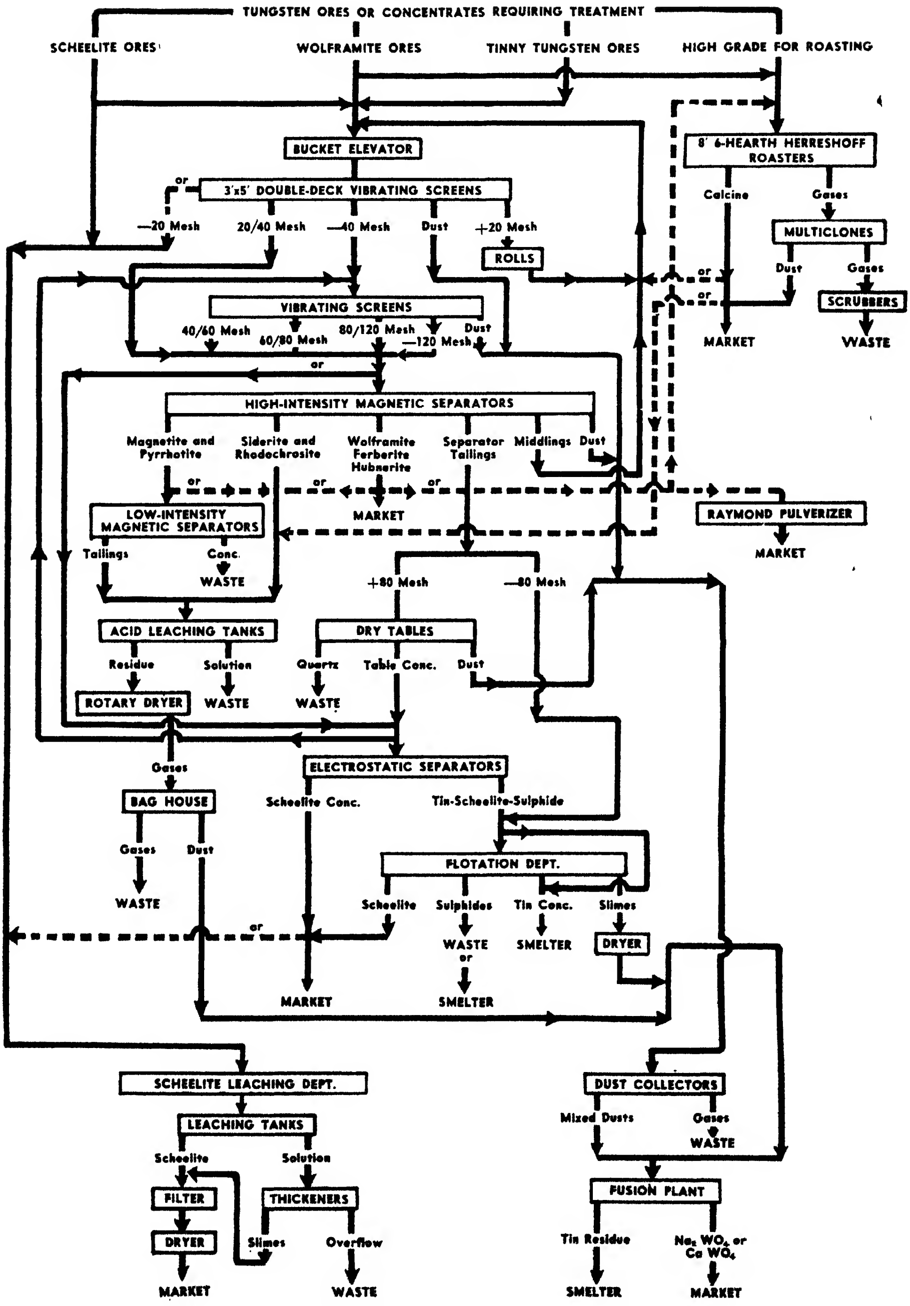
"The solutions are clarified, acidified and treated to remove molybdenum, after which the tungsten is precipitated with lime, washed and calcined in an Edwards furnace equipped with a bag house. The tungsten product is packed in steel drums containing approximately 275 lbs. Molybdenum is recovered as a by-product of this purification circuit, and is dried and shipped in steel drums."

(5) **Wah Chang's Plant for Concentrating Tungsten.***

Among the many mineral dressing plants of tungsten in this country and elsewhere this plant is unique. Its uniqueness lies in the fact that it does not produce concentrates from ores as mined but retreats concentrates or semiconcentrates from various tungsten mines in different parts of the world. Shipments have come to the plant from such widely scattered sources as China, Bolivia, Argentina, Peru, Brazil, Mexico, Belgian Congo, French Indo-China, Siam, Burma, the Malay States, Portugal, Spain and Canada as well as from all parts of the United States. This plant may thus be regarded as an ultra mineral dressing plant for tungsten concentrates, which was of verity born out of the desire on the part of the chairman

---

* *Eng. Min. J.*, 64–71, Sept., 1944.



Flowsheet of Wah Chang's plant for concentrating tungsten.

of the corporation to further the war effort by trying to meet the urgent demand for tungsten, one of the most important of the strategic metals.

The treatment plant itself comprises the following units:

A magnetic-separation plant with five large newly designed separators, having a capacity of 60 tons of concentrates per day.

An electrostatic separation plant.

A roasting plant with two Herreshoff furnaces, capable of handling 30 tons of concentrates per day.

A leaching plant with 8 tanks, two reconditioners, a drum filter and a series of filter presses and settling tanks, with an over-all capacity of 30 tons a day.

A flotation plant with a ball mill, thickening tanks, filter drums and press, able to treat 25 tons per day.

A drying plant and baghouse with a capacity of 24 tons per day.

A fusion plant complete with boilers, furnaces, tanks, crystallizers, dryers, capable of treating 10 tons per day.

A sizing and crushing plant to serve the roasting, leaching, fusion and separation departments.

The plant has a flexibility which makes it possible to produce refined tungsten concentrates of almost any type or specification. In this refining treatment major emphasis is placed upon the removal of impurities. The more detrimental impurities in tungsten concentrates are: sulfur, phosphorus, copper, tin, arsenic, antimony, bismuth, molybdenum, lead, tantalum and columbium. Silica and alumina are minor impurities. The effect of each of these impurities on finished tungsten products or on plant operation is given in the following table:

Effect of Impurities in Tungsten Concentrates on Finished Products or on Operations

Impurity	Effect
Sulfur	As FeS makes steel "red short".
Phosphorus	Makes steel "cold short".
Copper	Causes hot shortness. Also increases grain size of 13 per cent tungsten steel.
Tin	Reduces cutting efficiency of high-speed steel and in small amounts lowers toughness at room temperature.
Arsenic and Antimony	Cause exceptional hot and cold shortness and unusual brittleness of cutting edge. Antimony more serious than arsenic in reducing tool life of finishing cuts.
Molybdenum	Causes short life of filament wire and contacts, due to ease of volatilization and oxidation.
Tantalum and Columbium	Tantalum not serious if extraction of WO_3 is by sodium carbonate fusion or caustic soda leaching. However, if fusion or leaching is with potassium compounds, the potassium tantalate is soluble and its oxide will be precipitated with tungstic oxide.

Lead	Lead and arsenic fumes during smelting are poisonous.
Bismuth	Bi, Sn, Sb, As, and P interfere with control of particle sizes and other physical characteristics of WO_3, which affect quality of tungsten powder reduced from such WO_3.
Silicates and Alumina	Their presence and oxides of alkali and alkaline earth metals interfere with control of crystal structure of metallic tungsten and thus lead to brittle products.

Veins carrying tungsten minerals of the so-called black group usually contain at least minor amounts of most of the common sulfide minerals, with tourmaline, topaz, apatite, and (always) scheelite. Few purification problems arise, however, by reason of intimate intergrowths; because the black minerals occur generally as fairly large well-defined crystals.

Purification of the black or wolframite group of minerals is usually made easier because they are somewhat magnetic and are likely to be set free at comparatively coarse mesh sizes. Most ferberite, wolframite, and hübnerite concentrates produced originally by gravity concentration can be concentrated further by magnetic separation. They usually carry scheelite and cassiterite which go into the separator tailing with sulfides and gangue and call for further treatment, as by electrostatic separation and flotation. Leaching or roasting or both may be used to remove the last of such impurities as sulfur, arsenic, bismuth, phosphorus and antimony.

Scheelite ores usually carry fewer sulfides but frequently have them in relatively large amounts, plus phosphorus, arsenic, antimony and molybdenum.

The flow sheet shows the steps of the batch-processing of the tungsten concentrates.

In the magnetic separation department, as elsewhere, the hoppers of the machines are filled by means of transfer cans and the monorail hoist, the products being received in steel drums of 2 cubic feet capacity. To what has been said in connection with the picture of the separators, it may be added that the magnetic products of the belts are discharged into split chutes so that weakly-magnetic particles and coarse minerals mechanically brushed from the main belt are caught in the first section of the chute and returned for crushing.

The strongly magnetic products usually contain sufficient values to warrant further treatment. The magnetite and pyrrhotite may be cleaned in low-intensity separators, if the valuable minerals are merely entangled. But where tungsten and tin present are due to surface contamination, the concentrates are leached with sulfuric or hydrochloric acid, dried, and returned.

Iron and manganese carbonates are only slightly more magnetic than wolframite, and an important quantity of tungsten is ordinarily found in the product containing them. This may be separated by dry tabling the coarse sizes and acid-leaching the fine sizes. Wolframite concentrates containing soluble impurities, or those which can be made soluble by roasting (as bismuth), are also leached.

In leaching scheelite, phosphorus is removed with hydrochloric acid. Calcite and dolomite, commonly found in flotation concentrates, are also removed by leaching. Bismuth present as oxide is likewise acid-soluble. Sulfides of arsenic and antimony are removed by leaching with caustic soda.

Each leaching cycle is followed by settling and decantation of the waste solutions. The product is finally washed and discharged to an agitator tank feeding an Oliver filter, which delivers its cake into an indirect-heat, helical screw drier.

Decanted solutions are discharged to standard thickeners, one steel tank for alkali solutions, and one wood tank with wood mechanisms for acid solutions. Settled slimes are periodically returned to leaching by Oliver slurry pumps. Overflow is filtered through Shriver plate-and-frame presses and sent to waste. The small amount of solids caught in the presses joins the underflow for re-leaching.

Close control of the acid leaching cycle is important, as small increases in the strength of the final acid solutions may cause prohibitive WO_3 losses. Solubility of scheelite in hydrochloric acid will depend upon the characteristics of the material leached, the size, and the impurities. For instances, if the scheelite contains much calcite, as it often does, the heat generated by the reaction affects the solubility of the scheelite. At the same time the free acid in the tanks must be between 1 and 2 per cent to ensure removal of phosphorus. Somewhat higher concentrations are necessary in the bismuth leach to prevent hydrolysis to bismuth oxychloride and consequent re-precipitation.

References

1901

1. **Hobbs, W. H.**, "The Old Tungsten Mine at Trumbull, Conn.", U. S Geological Survey, 22nd Annual Report, 7-22 (1901).

1903

2. **Skewes, E.**, "Magnetic Separation of Tin and Wolfram at Gunis-lake Clitters, Cornwall", *Eng. Min. J.*, **76**, 424 (1903).

1905

3. **Wagenen, H. R. von**, "Tungsten in Colorado", Frenzel Prize Thesis, Colorado School of Mines (1905).

1906

4. **Dietzsch, F.**, "Concentration of Tin and Tungsten in Cornwall", *Trans. Inst. Min. Met., London*, 15, 2 (1906); Abs.: *Min. J.*, **78**, No. 3662; *Eng. Min. J.*, **83**, 112 (1907).
5. **Wagenen, H. R. von**, "Concentration of Colorado Tungsten Ores", *Bull. Colo. School Mines*, **3**, 138 (1906); Abs.: *Min. Mag.*, **13**, 327 (1906).

1907

6. **Treloar, A.**, and **Johnson, G.**, "The Separation of Tin Oxide from Wolframite", *Elektroch. Zeit.*, **16**, 10 (1907); *Trans. Inst. Min. Met., London*, **17**, 137-58 (1907-08).

7. Walker, E., "The Ore Dressing Plant, East Pool, Cornwall", *Eng. Min. J.*, **83**, 941 (1907).

1908

8. Gee, H. H., and French, S. W., "Magnetic Versus Hydraulic Concentration of Tungsten Ores", *Min. Sci. Press.*, **57**, 591-592 (1908); **58**, 9-10 (1908).

9. Terrell, L. L., "Final States of Tin and Wolfram Dressing", *Min. J.* (*London*), 714-15 (June 13, 1908).

1909

10. Gunther, C. Y., Separation of Wolframite From Tin Ore, "Electro-magnetic Ore Separation", pp. 168-70, McGraw-Hill Book Co., New York, 1909.

11. Hills, V. G., "Tungsten Mining and Milling", *Proc. Colorado Sci. Soc.*, **9**, 135-153 (1908-1911); *Min. World*, **30**, 1021-4, (1909)

12. Wood, H. W., "Notes on the Magnetic Separation of Tungsten Minerals", *Proc. Colo. Sci. Soc.*, **9**, 154-8 (1909); *Min. World*, **30**, 968 (1909)

13. Anon., "The Murex Magnetic Process", *Mining Mag.*, 142-3 (1909)

1910

14. Paddock, C. H., "Tungsten Milling in Boulder County, Colo," *Min. Scient. Press.*, **62**, 172-174 (1910).

1911

15. Freise, F., "Mill and Laboratory Practice in Dressing of Gold Ores, Monazite, and Wolframite", *Oesterr, Zeit. Berg-Huttenw.*, **59**, 284 (1911)

16. Longbottom, W. A., "Scheelite Mining", *Australian Min. Eng. Rev.*, **3**, 200 (1911).

17. Mennicke, H., "Separation of Tungsten from Tin Ores and Tin Slags", *Monograph of Applied Electrochemistry*, **39**, 138 (1911)

18. Parmelee, H. C., "The Problems of Tungsten Concentration", *Met. Chem. Eng.*, **9**, 341-343 (July, 1911); 409-411 (Aug., 1911); *Can. Min. J.*, **32**, 458 (1911).

19. Watts, H. F., "Notes on the Analysis of Tungsten Ores", *Met. Chem. Eng.*, 414-415 (Aug., 1911)

1912

20. Pickerings, H. B., "Tungsten Milling Practice of Nova Scotia", *Min. Eng. World*, **37**, 60 (1912)

21. Russell, M., "Scheelite Mining in New Zealand", *Queensland Govt. Min. J.*, **13**, 116 (1912).

1913

22. Ackerman, E., "The Concentration of Tungsten Ores", *J. Mines and Met.*, **1**, 162-163 (1913).

23. Becket, F. M., "Process of Treating Tungsten Ores", U. S. Pat. 1,081,566 (1913).

24. Falkenberg, O., "Treatment of Tinstone and Wolframite", *Min. J.* (Aug. 23, 1913).

25. Hills, V. G., "A Tungsten Mine in Nova Scotia", *Min. Scient. Press*, **106**, 448-450 (1913).

26. Palmer, L. A., "Tungsten in Boulder County, Colorado", *Eng. Min. J.*, **96**, 99 (July 10, 1913).

1914

27. Freise, F., "Experiments in Concentrating Monazite and Wolframite", *Metall u. Erz.*, **11**, 573-8, 587-94 (1914).

28. Gudgeon, C. W., "Scheelite Mining in New Zealand", *Australian Min. Standard*, **50**, 409 (1914).

29. Hills, L., "Treatment of Tin-Wolfram-Bismuth Ores", *Min. Eng. Rev.*, (July 16, 1914); *Eng. Min. J.*, **98**, 486 (1914).

30. Hyde, J. M., "The Murex Process in a German Works", *Min. Scient. Press* (June 6, 1914).

1915

31. Becket, F. M., "Method of Treating Tungsten Ores", U. S. Pat. 1,153,594 (1915).

32. Lefroy, E. M., "Wolframite Mining in the Tavoy District, Lower Burma", *Trans. Inst. Min. Met.*, **25**, 83-107 (1915).

33. Savage, F. A., "Mining and Concentrating Tungsten Ore in Bolivia", *Compressed Air Mag.*, **21**, 7877 (1915).

34. Taylor, M. T., "Separation of Wolfram from Tin", *Min. Mag.*, **12**, 351-2 (June, 1915).

35. Vogel, F. A., "Magnetic Separation of Tin-Wolframite-Bismuth Ores", *Eng. Min. J.*, **99**, 287 (1915).

1916

36. Fleck, H., "Concentration of Tungsten Ore", *Min. Sci. Press*, **112**, 156 (1916).

37. Grossbert, A., "Separating Wolframite from Tin", *Eng. Min. J.*, **102**, 139-40 (1916).

38. Hills, V. G., "Tungsten Mining and Milling", *Eng. Min. J.*, **102**, 126-7 (1916).

39. Leslie, E. H., "Tungsten in the Boulder District, Colorado", *Min. Scient. Press.*, **113**, 353-355 (1916).

40. Magee, J. F., "The Milling of Tungsten Ores (Colorado)", *Eng. Min. J.*, **101**, 717-8 (1916).

41. McDonald, P. B., "Tungsten Mining in the West", *Min. Scient. Press*, **112**, 757 (1916).

42. Miner, F. L., "The New Milling Plant for the Nevada, Tungsten Property", *Min. Eng. World*, **44**, 1078 (1916).

43. Parmelee, H. C., "Recent Practice in Concentrating Colorado Tungsten Ores", *Met. Chem. Eng.*, **14**, 301-304 (March 15, 1916).

44. Robertson, A. J., "On Concentration Tests of Tungsten-Molybdenum Ores from Callie Creek, Poona, Murchison Goldfields", Geol. Surv. West. Aust., Bull. 64 (1916).

45. Scott, W. A., "Concentrating Tungsten Ores, Boulder County, Colorado", *Min. Eng. World*, (*Chicago*), **45**, 697-701 (Oct. 21, 1916).

46. Wolf, H. J. and Barbour, P. P., "The Boulder County Tungsten District, Colo", *Eng. Min. J.*, **102**, 165-169 (July 22, 1916).

1917

47. Fischer, S., "Modern Concentration Colorado Tungsten Ores", *Met. Chem. Eng.*, **16**, 559-565 (1917); **17**, 73-78 (1917).

48. Miller, J., "Treatment of Tin-Wolfram Ore, Storey's Creek Mine, Tasmania", *Chem. Eng. Min. Rev.*, **10**, 467-8 (Dec., 1917). Abs.: *Chem. Met. Eng.*, 261 (Sept. 1, 1918).

49. Travers, M., "A New Separation of Tin and Tungsten in Stanniferous Wolfram", *Compt. rend.*, No. 165, 408-410 (1917).

50. Anon., "Boulder Colorado Milling Practice", *Met. Chem. Eng.*, **17**, 73, 207 (1917).

51. Anon., "Flow Sheet of Round Valley, California, Tungsten Mill", *Eng. Min. J.*, **104**, 925 (1917).

52. Anon., "East Pool Dressing Practice", *Min. Mag.*, **17**, 281-282 (1917).

53. Anon., "Improvements in Tungsten Recovery", *Met. Chem. Eng.*, **17**, 207 (1917).

1918

54. Bland, G. V., "On Ferberite", *Eng. Min. J.*, **105**, 908 (1918).

55. Goodrich, R. R. and Holdern, N. E., "Experiments in the Recovery of Tungsten and Gold in the Murray District, Idaho", *Amer. Inst. Min. Eng.*, **58**, 224 (1918).

56. Stutzer, F., Cross, W., and Bornemann, K., "Ueber magnetische Eigenschaften der Zink-blend unde einiger anderer Mineralien", *Metall u. Erz.*, **15**, 1 (1918).

57. Anon., "Concentrating a Tin-Wolfram-Lead Ore", *Chem. Eng. Min. Rev.*, Melbourne, (June 5, 1918), Abs.: *Min. Scient. Press*, 162 (Aug. 3, 1918).

58. Anon., "Triple Concentration Practice for Tin-Wolfram-Lead Ore", *Eng. Min. J.*, 530-1, (Sept. 21, 1918).

1919

59. Hitchcock, W. E., "Treatment of Bismuth, Tin and Wolfram Ores", *Proc. Aust. Inst. Min. Met.*, **35**, 33-73 (1919); Abs.: *J. Soc. Chem. Ind.*, 175A (March 15, 1920); *Min. Mag.*, 175-9 (March 20, 1920).

60. Weigall, V. A. R., and Mitchell-Roberts, J. F., "Technical Operations on the Suan Concession, Korea", *Min. Scient. Press*, 915-24 (Dec. 27, 1919).

61. Anon, "Water Concentration at Storey's Creek, Tasmania", *Chem. Eng. Min. Review* (Dec., 1919).

1920

62. Bowater, "Bismuth-Wolfram-Molybdenum Separation", *Proc. Aust. Inst. Min. Met.*, No. 40, (1920), Abs.: *Min. Mag.*, 182 (Sept. 1921).

63. Hitchcock, W. E., and Pound, J. R., "Mining and Milling Tin-Tungsten Ore in Tasmania", *Min. Scient. Press*, 229-231 (Feb. 14, 1920).

64. Matignon, Camille, "Le Tungstène", *Chimie et Industrie*, **3**, No. 3, 72T-75T (March, 1920).

65. Sington, T., "Reducing Tungsten Ore", *Eng. Min. J.*, **109**, 879-80 (April 10, 1920).

66. Webster, Edser and Wood, "To Prevent Losses in Flotation", Dutch Pat. No. 5482 (1920).

1921

67. Bonardi, J. P., and Williams, J. C., "Treatment of Tungsten Ores of Boulder County, Colorado", U. S. Bureau of Mines, Bull. No. 187 (1921).

68. Lavers, H., "Notes on Tungsten, with Particular Reference to King Island Scheelite Treatment and Assays of Low-Grade Material", *Proc. Aust. Inst. Min. Met.*, No. 43, 101-52 (1921); Abs.: *Min. Scient. Press*, 821-4 (Dec. 10, 1921).

69. Anon., "Dressing of Wolfram Ores in Queensland", *Min. Mag.*, 182-185 (Sept. 1921).

1923

70. Brown, J. C., and Heron, A. M., "Concentrating Mills", Geology and Ore Deposits of the Tavoy District, *Memoirs of the Geol. Survey of India*, **44**, Part 2, 312-316 (1922).

1927

71. Osborn, W. X., "Tabling Tungsten Ores Without Water", *Eng. Min. Journ.*, **123**, 287-9 (1927).

1929

72. Bonardi, J. P., and Boericke, W. F., "Tungsten Milling In Colorado", *Min. Met.*, **10**, 200-203 (April, 1929).

73. Doener, H. A., "Centrifugal Concentration", U. S. Bureau of Mines, Technical Paper 457, 38-39 (1929).

1930

74. Heizer, O. F., "Methods and Costs of Concentrating Tungsten Ore at the Nevada-Massachusetts Mill, Mill City, Nevada", U. S. Bureau of Mines, Inf. Cir. 6284 (June, 1930).

75. Shukin, I. A., "Ore enrichment of Tungsten, Belukhinsk and Bukukinsk Origin", *Mechanobr, (Inst. of Ore Dressing), USSR*, 78 144 (L-1930).

1931

76. Brennan, J. H., "Removing Arsenic from Ores", U. S. Pat. 1,790,088 (1931).

77. Huttl, J. B., "Tungsten Mining and Milling", *Eng. min. J.*, **131**, No. 9, 405-406, (May 11, 1931); *Eng. Min. World*, **2**, 351-2, (June, 1931).

78. Vandenburg, W. O., "Methods and Costs of Concentrating Tungsten Ores at Atolia, San Bernardino County, California", U. S. Bureau of Mines, Inf. Cir. 6532 (Oct. 1931).

1932

79. Vandenburg, W. O., "Methods and Costs of Concentrating Scheelite Ore at the Silver Dyke Mill, Mineral County, Nevada", U. S. Bureau of Mines, Inf. Cir. 6604 (April, 1932).

1933

80. Vandenburg, W. O., "Methods and Costs of Milling Ferberite Ore at the Wolf Tongue Concentrator, Nederland, Boulder County, Colorado", U. S. Bureau of Mines, Inf. Cir. 6685 (Jan., 1933).
81. Clemmer, J. B., and O'Meara, R. G., "Flotation and Depression of Nonsulphides: Fluorspar, Barite, Apatite and Tungsten Minerals", U. S. Bureau of Mines, Rept. of Invest. 3239 (June, 1934); Abs.: *Min. J.*, 675, 676 (Sept. 8, 1934); 691 (Sept. 15, 1934); 709, 710 (Sept. 22, 1934).
82. Dean, R. S., and Davis, C. W., "Magnetic Concentration of Ores", *Trans. Amer. Inst. Min. Met. Eng.*, 509-537 (1934).
83. Coghill, W. H., and Clemmer, J. B., "Soap Flotation of the Nonsulphides", *Trans. Am. Inst. Min. Met. Eng.*, **112**, 459 (1934).
84. Heizer, O. F., "Concentration of Tungsten Ore by the Nevada-Massachusetts Co", *Trans. Am. Inst. Min. Met. Eng.*, **112**, 833-40 (1934).
85. Patek, J. M., "Flotation Treatment of Nonsulphidic Ores", U. S. Pat. 1,954,431 (April 3, 1934).
86. Yasyukevich, S. M., "Experiment on Scorodite Flotation", *Tzvetnye Metal*, No. 7, 26-35 (1934).

1934

87. Heizer, Otto F., "Concentration of Tungsten Ore by the Nevada-Massachusetts Company", *Trans. Am. Inst. Min. Met. Eng.*, **112**, 833-840 (1934).

1935

88. Vandenburg, W. O., "Mining and Milling Tungsten Ores", U. S. Bureau of Mines, Inf. Cir. 6852 (Sept., 1935).
89. Winkler, M., "Ein Beitrag zur Flotation von Zinnstein and Wolframit", *Metall und Erz.*, 181-183 (May, 1935).

1936

90. MacAfee, M. W., "Concentrating Ores and Minerals by Flotation", U. S. Pat. 2,060,815 (Nov. 17, 1936).
91. Gorodetskii, M. I., "The Flotation of Scheelite", *Gorno-Obogatitel Zhur*, No. 4, 37-38, (1937).
92. Hope, G., "Scheelite Mining in New Zealand", *Chem. Eng. Min. Rev.*, 13-15 (Oct. 14, 1937).
93. Jarman, G. W., "Special Methods for Concentrating and Purifying Industrial Minerals", *Am. Inst. of Min. Met. Eng., Technical Publication No. 969* (1937).
94. Ralston, O. C., "Froth Flotation and Agglomerate Tabling of Non-metallic Minerals", *Trans. Canadian Inst. of Min. Met.*, **40**, 691-726 (Nov., 1937).
95. Anon., "Tungsten Production", *Chem. Eng. Min. Rev.*, 445-448 (Sept. 20, 1937).
96. Rose, E. H., and MacDonald, W. T., "Process for Separating Solids by Flotation", U. S. Pat. 2,040,187 (May 12, 1936).

1937

97. Handy, R. S., "Flotation Reagent", U. S. Pat. 2,069,365 (Feb. 2, 1937).

1938

98. Dennowa, O. A., "Scheme for getting the Conditioned Tungsten Concentrate from the Complex Ore of Kalyvan Deposit", *Tsvetnye Metal*, No. 10, 77 (1938).
99. Gulyayer, S., "Flotation of Scheelite Concentrate of Tuimsk Factory", *Tsvetnye Metal*, No. 8, 37 (1938).
100. Johnson, H. B., "Selective Electrostatic Separation", Am. Inst. Min. Met. Eng., Technical Publication No. 877 (1938).
101. Leaver, E. S., and Royer, M. B., "Flotation for Recovery of Scheelite from Slimed Material," U. S. Bureau of Mines, Technical Paper 585 (1938).
102. O'Malley, G. B., "Tin-Tungsten Mining at Aberfoyle", *Chem. Eng. Min. Rev.*, 303-310 (May 10, 1938).
103. Paull, C. V., "Wolfram in Cornwall", *Mine Quarry Eng.*, 99-104 (March, 1938).
104. Ralston, O. C., "Flotation and Agglomerate Concentration of Nonmetallic Minerals", U. S. Bureau of Mines, Rept. of Invest. 3397 (1938).
105. Anon., "Flotation of Scheelite", U. S. Bureau of Mines, Rept. of Invest. 3419, 62-63 (Oct., 1938).
106. Anon., "Silver-Lead-Tungsten Ore from the Regal Silver Property, Near Revelstroke, British Columbia", Ore Dressing and Metallurgical Investigation No. 756, Bureau of Mines, Ottawa (1938).

1939

107. Barton, W. P., and Arentz, Jr., S. S., "Mining & Milling at Ima Mine", *Min. Cong. J.*, **25**, No. 8, 16-19 (Aug., 1939).
108. Belash, F. N., and Pugina, O. V., "Experiments in Flotation of Sulphide-Hübnerite Ores", *Tsvetnye Metal*, No. 7, 72-75 (1939).
109. Deminova, O. A., "Utilization of Lean Tungsten Ores", *Tsvetnye Metal*, No. 7, 48-50 (1939).
110. Glembotsku, V. A., "Method of Ore Testing by Magnetic Separation", *Tsvetnye Metal*, No. 8, 44-6 (1939).
111. Gulyaev, S. I., "Recovery of Tungsten Minerals in the Process of Hydraulic Separation", *Tsvetnye Metal*, No. 12, 64-6 (1939); *Khim Referat Zhur*, No. 5, 93-4 (1940).
112. Pearson, A., "Sink and Float at Halkyn Mill", Paper presented to the Inst. of Min. Met., London (June 15, 1939); Abs.: *Min. J.*, 651-653 (July 8, 1939); 720, (July 29, 1939); Brit. Pat. 486, 771 (June 8, 1938).

113. Anon., "Plants for Mechanical Enrichment of the Tungsten ores at Dzhidinsu Deposit", *Tsvetnye Metal*, No. 8, 35 (1939).

114. Anon., "Ima Mine", *Bull. M4-B-13*, Denver Equipment Co. (1939)

1940

115. Denyer, J. E., and Heath, K. C. G., "Mining and Milling Tin Tungsten Ore at Mawchi Mine, Burma", *Inst. Min. Met., London* (March, 1940).

116. Norton, C. C., "Bamford Wolfram-Molybdenite-Bismuth Mines", *Queensland Govt. Min. J.*, **41**, 40 2 (Feb., 1940).

117. Polkin, C. I., and Olunina, N. I., "Flotation of Oxidized minerals (Scorodite and wolframite)", *Tsvetnye Metal*, No. 12, 36–44 (1940).

118. Rosov, B. I., and Miasnikova, G. A., "Flotation of Scheelite from Ores of Tyrnyans Deposits", *Tsvetnye Metal*, No. 4, 33 41 (1940)

119. Anon., "Flotation of Oxidized Minerals (Scorodite and Wolframite)", *Tsvetnye Metal*, 36 (Dec., 1940)

120. Anon., "Latest Practice in Scheelite Recovery (Gravity Table and Flotation)", *Chem. Eng. Min. Rev.*, (*Melbourne*), **32**, 238 9 (March 11, 1940)

121. Anon., "Scheelite Stibnite Ore from the Bridge River Area, British Columbia", Ore Dressing and Metallurgical Investigations No. 859, Bureau of Mines, Ottawa (1940).

1941

122. Burwell, B., "Milling Tungsten Ore at Pine Creek", *Min. Cong. J.*, **27**, No. 10, 16-18 (1941).

123. Lenhart, W. B., "Milling Scheelite at Tungsten Mine", *Min. Cong. J.*, **27**, 67-71 (April, 1941).

124. Anon., "Magnetic Separation", Stearns Magnetic Mfg. Co., Milwaukee, Wis., Bull. 80 and 101 (1941)

125. Bruder, Charles, "Mining Tungsten, Gold and Copper at Outpost Island, Northwest Territories", Manitoba Chamber of Mines, **2**, (Feb., 1941).

126. Gulya'ev, S. I., "The Extraction of Scheelite on the Deiser Slime Table", *Tsvetnye Metal*, **16**, No. 2-3, 43 4 (1941), *Chem. Zentr.*, **II**, 2309-10 (1942).

1942

127. Burdick, E. H., "Benefication of Scheelite Ores by Gravity Concentration", Tech. Pub. No. 1534, *Am. Inst. Min. Met. Eng.*, "Mining Technology" (November, 1942).

128. Eardley-Wilmot, "Tungsten Canadian and World Situation", *Trans. Canadian Inst. Min. Met.*, **45**, 437–454 (Bull. No. 367, 1942).

129. Koulomzine, T., "Recovery of Scheelite from Gold Ore Containing only 0.001 per cent Tungsten at Central Cadillac Mines, Western Quebec", *Canadian Min. Met. Bull. Montreal*, No. 366, 479 82 (October, 1942).

130. McLaren, D. C., "Tungsten, an Important War Metal", *Mining Cong. J.*, 29–33 (July, 1942)

131. McLaren, D. C., "Tungsten in Canada", *Eng. Min. J.*, **143**, No. 10, 55–59 (October, 1942)

132. Munds, W. H., "Mining and Milling Tungsten Ores at Borianas", *Mining Cong. J.*, 14–16 (September, 1942).

133. Anon., "American Practice in Scheelite Concentration; Gravity and Flotation Favoured", *Chem. Eng. & Min. Review, Melbourne*, **34**, 117-119 (January, 1942)

134. Anon., "M B I Sink and Float Process", The American Zinc, Lead & Smelting Company, St. Louis, Missouri (1942).

135. Anon., "Vanadium, Tungsten and Chromium", *Mining Cong. J.*, 50–52 (Feb., 1942)

136. Anon., "Flotation Tests on Scheelite Bearing Chalcopyrite Ore from Beaverhouse Lake Gold Mines, Ld., Gauthier Township, Ontario", Canada Dept. of Mines and Resources, Mines and Geology Branch, Bureau of Mines, Rept. 1294 (Sept., 1942).

137. Anon., "Opening Body of Tungsten, Oregon", *Mining World, Seattle*, 3-6 (Feb., 1942).

138. Hamilton, R., "Tungstar's Recovery of Scheelite", *Min. J., Arizona*, 6 (Feb., 1942).

139. McLaren, D. C., "The Beneficiation of Canadian Tungsten Ores", *Min. Mag., Lond.*, 299 308 (Dec., 1942); *Min. J., London*, 338-339 (July 10th, 1943)

140. Miller, H. H., "Tungsten Mining in Idaho", *Min. J., Arizona*, 3-4 (Aug., 142).

1943

140a. Dice, C. M., "Methods and Costs of Concentrating Hübnerite Ores at the Ima Tungsten Mine, Lemhi County, Idaho", U. S. Bureau of Mines, Inf. Cir. 7230 (Jan., 1943).

141. Belash, F. N., "Flotation of the Tungsten Ores of Bukuki", *Tsvetnaya Metal*, **16**, No. 13, 16-20 (1943); *Chem. Zentr.*, **I**, 1927–8 (1943).

142. Blackshaw, John, "The Recovery of Scheelite Concentrate at Hollinger Tungsten Mill", *Trans. Can. Quat. Min. Met.*, 46-226-56 (*Can. Min. Met. Bull. No. 375*) (1943).

143. Cummings, J. M., "Beneficiation of Some British Columbia Tungsten Ores", *The Miner, Vancouver*, 27-30 (May, 1943); 45-50 (June, 1943).

144. Cummings, J. M., "Tungsten Deposits of British Columbia", British Columbia Dept. of Mines Revised Bull. No. 10, 23-26 (1943).

145. Cummings, J. M., "Benefication of Some British Columbia Tungsten Ores", *Canadian Min. Met. Bull.*, 47–69 (Feb., 1943).

146. Dennis, W. H., "Tungsten (Gravity Methods, Flotation)", *Mine Quarry Engineering*, **8**, 81–82 (April, 1943).
147. Huttle, John B., "Spud Patch Tungsten Placer Proves Commercial Venture", *Eng. Min. J.*, 94–96 (Dec., 1943).
148. Knapp, E. A., "The Flotation Cell Feed", *Mining Mag., Lond.*, 325–337 (June, 1943).
149. Matthews, W. H., "Scheelite and Powellite", *The Miner, Vancouver*, 33–35 (March, 1943).
150. McLaren, D. C., "Notes on the Treatment of Slimed Tungsten Ores", *Mining Mag., Lond.*, 201–206 (April, 1943).
151. Melzer, R., and Popperle, J., "Flotation of Oxidic Ores, particularly Sn-W Ores", German Pat. 736,520 (May 13, 1943).
152. Reck, W. H., "Boulder Tungsten Mills, Inc.", Deco. Trefoil, Denver Equipment Co., 5–12 (Oct., 1943).
153. Segerstrom, C. H., "Tungsten Mining and Ore Dressing Greatly Advanced", *Mining Cong. J.*, 32–34 (Feb., 1943).
154. Voorhis, B. W. von, "How Getchell Treats Tungsten, Arsenic and Gold Ores in its Remodeled Mill", *Mining World*, **5**, No. 3, 9–13 (1943).
155. Anon., "Flotation of Tungsten Ores", *Mining J., Lond.*, 238 (July 10, 1943).
156. Anon., "Flotation of Ferberite, Wolframite and Hubnerite", *Mining J., Lond.*, 339 (July 10, 1943).
157. Anon., "Ore Dressing Notes, Concentrating Scheelites", *Mining Mag., Lond.*, 344–347 (June, 1943).
158. Anon., "Tungsten Ores and Concentrates", *Can. Min. J.*, **64**, 164–6 (March, 1943).
159. Anon., "Dredging Tungsten in California's Mojave Desert", *Mining J., Lond.*, 375–6 (July 31, 1943).

1944

160. Crozier, L. A., "Wolfram Mining in Jodhpur", *Chem. Eng. Min. Rev., Melbourne*, 218–26 (May, 1944).
161. "Wolfram Mining and Milling in Jodhpur, India", *Chem. Eng. Min. Rev., Melbourne*, 318–26 (May, 1944).
162. Falconer, S. A., and Crawford, B. D., "Froth Flotation of Some Nonsulphide Minerals of Strategic Importance", *Mining Technology*, Technical Publication No. 1754, Am. Inst. Min. Met. (Nov., 1944).
163. Garcia, L. G., "Government Tungsten Mill Aids Mining in Peru", *Eng. Min. J.*, 79 (April, 1944).
164. Hall, R. G., "Recovery of Tungsten from Its Ores", U. S. Pat. 2,351,678 (June 20, 1944).
165. Nevett, R. D., "Wilks Creek Wolfram Mine (Victoria) Concentrating Practice, Reduction by Rolls, Vibrating Screen Instead of Hydraulic Classification", *Chem. Eng. Min. Rev., Melbourne*, **37**, 38–42 (November 10, 1944).
166. Anon., "Treatment of King Island Scheelite: Investigational Work, Roll Crushing and Jigging, Tabling and Flotation for Finer Sizings", *Chem. Eng. Min. Rev., Melbourne*, **36**, 299–305 (August, 1944).
167. Anon., "Separation from the Ore of Molybdenum and Tungsten", *Min. J., London*, 297 (May 20, 1944).
167a. Anon., "Wah Chang's Unique Plant for Concentrating Tungsten", *Eng. Min. J.*, 64–71 (Sept., 1944).

1945

168. Gieseke, E. W., "Tungsten Ore flotation", U. S. Pat. 2,373,305 (April 10, 1945).
169. Taggart, A. F., "Handbook of Mineral Dressing", p. (2) 243–250, John Wiley & Sons, N. Y.
170. Anon., "Nevada Tungsten Ore Gets Three Way Treatment", *Eng. Min. J.*, 81–85 (July, 1945).

Chapter IV

The Metallurgy of Tungsten

The metallurgy of tungsten is unique in that, because its melting temperature (3410° ± 20°C)* is the highest of all known metals, it cannot be handled like ordinary metals. Hence, treatment of the ore for the production of metallic tungsten involves processes whereby intermediate products are first obtained. The usual intermediate product is tungstic acid, although other intermediate products, like tungsten chloride, have been proposed. Metallic tungsten is then produced in powder form from treating this intermediate product.

The metallurgy of tungsten, as it is today is largely empirical and is mainly based upon patents. Patents are keys to the technology of tungsten; therefore, in large measure, they are the source of material in the treatment of this subject.

The various methods and processes that have been proposed or adopted for the treatment of tungsten ores may be discussed under the following classifications:

I. Decomposition of Tungsten Ore

1. With sodium or potassium carbonate
2. With sodium nitrate
2. With alkali hydroxide
4. With ammonia
5. With fused alkali
6. With hydrosulfate
7. With calcium carbonate and sodium chloride
8. With neutral salts
9. With acids
10. As chloride
11. By electrolysis
12. By volatilization
13. As sulfide
14. With hydrogen sulfide

---

* U. S. Bureau of Standards.

II. Purification of Tungstic Oxide

1. Precipitation as tungstic acid
2. Crystallization as ammonium paratungstate
3. Precipitation as calcium tungstate
4. Treatment with magnesium salts
5. As tungsten sulfide
6. Treatment with benzidin-hydrochloride
7. Treatment with ferro-silicon
8. As tungsten oxy-tetrachloride

III. Production of Tungsten Powder

1. Reduction of tungstic oxide with hydrogen
2. Reduction of tungstic oxide, tungstates, or tungsten ore with carbon
3. Reduction of tungstic oxide or tungsten ore with metals or their compounds
4. Treatment of tungsten sulfide
5. Treatment of tungsten chloride
6. Electrolysis
   a. From solution
   b. From fused bath
7. By thermal decomposition

I. DECOMPOSITION OF TUNGSTEN ORE

1. With Sodium or Potassium Carbonate

The process, patented in 1847 by Robert Oxland (British Patent 11,848) for the extraction of tungstic acid by first fusing wolframite ore with soda and then treating the sodium tungstate liquor with hydrochloric acid has formed the basis upon which the structure of the development of the metallurgy of tungsten rests.

The process now used for the treatment of wolframite ore has been described in detail by C. H. Jones.[1] The ground ore, after being mixed with soda ash in a ratio of one part of WO_3 content to one part of Na_2CO_3 plus a 15 per cent excess of soda ash, is ball-milled to pass 100-mesh screen. The fine mixture is then charged into a gas-fired reverberatory furnace and is continuously hand-rabbled at a temperature of about 800°, so as to allow free access of air to oxidize completely the iron and manganese content of the ore. The reactions which take place are represented by the following equations:

$$2FeWO_4 + O + 2Na_2CO_3 \rightarrow 2Na_2WO_4 + Fe_2O_3 + 2CO_2$$

$$3MnWO_4 + O + 3Na_2CO_3 \rightarrow 3Na_2WO_4 + Mn_3O_4 + 3CO_2$$

The operation requires about 2 hours for a charge of about 200 lbs of ore and 100 lbs of soda ash. The cooled mass from the furnace, after being crushed to pea size, is treated for the extraction of sodium tungstate with water under agitation for a long time, usually overnight to assure complete dissolving. The saturation of the solution is tested to read 50° Baumé and is not allowed to go below 30° Baumé.

As a modification of the above process, Ekeley and Stoddard (British Patent 122,051 [1919]) proposed the addition of sodium chloride to the fusion mixture. The sodium chloride performs the function of a solvent and diluent for the sodium carbonate and acts as an accelerator for a more rapid disintegration of the ore. "The extreme fluidity of the sodium carbonate and sodium chloride when fused together renders it possible also to use less of the sodium carbonate than when the sodium chloride is omitted." Instead of sodium chloride, the use of sodium fluoride or calcium chloride or fluoride may serve the same purpose. Sodium nitrate or sodium chlorate may be added as an oxidizing agent in the melt to facilitate the necessary action of oxidizing the iron and manganese content of the ore. Some ore requires the addition of silica, in the form of sand, to ensure the separation of calcium as calcium silicate.

For a large-scale operation to carry out the fusion in a continuous manner, a process has been patented by the General Electric Company (British Patent 189,873 [1922]) and another, similar process by F. M. Dorsey (U. S. Patent 1,535,019 [1929]). The outline diagram, shown on p. 162, shows the arrangement of the apparatus.

The fusion mixture, composed of 1080 lbs of wolfram ore, containing 70 per cent of WO_3, 375 lbs of sodium carbonate and about 45 lbs of Chile saltpeter, containing about 95 per cent of sodium nitrate, is fed at a rate of about 255 lbs per hour into the rotatory furnace which is heated to a temperature of between 980 and 1000° by a gas and air mixture. The pasty mass flows in a continuous manner into the lixiviating or dissolving tank. Wash water or wash liquor is fed into the tank at the rate of 55 gallons per hour. The material in the dissolving tank overflows and is fed to an Oliver continuous filter. The main filtrate has a specific gravity of 1.51 at 80°. To the solution of sodium tungstate is added a saturated sodium nitrate solution in the proportion of approximately 1 pound of sodium nitrate to 25 lbs of WO_3. The function of the added sodium nitrate is to decrease the solubility of the tungstic acid formed during precipitation operation and to ensure that the tungstic acid precipitated is yellow.

The solution is then heated to about 98 or 99°C before it is fed into the stoneware precipitating vat. The object in preheating the sodium tungstate solution is to prevent the formation in the precipitating vat of a white precipitate, which is more soluble in water, tends to absorb more impurities and is less crystalline and therefore more difficult to wash without becoming colloidal.

The 22° Baumé hydrochloric acid used in the precipitating vessel is heated to about 103 or 104°, and is always maintained at a 150 per cent in excess of the theoretical requirement. The reactions which probably take place are indicated as follows:

$$Na_2WO_4 + 2HCl \rightarrow H_2WO_4 + 2NaCl$$

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

The precipitated tungstic acid is then washed three or four times with a 0.3 per cent by volume solution of white nitric acid. This washing removes the chlorides from the precipitate, but the yellow precipitate is not affected by the nitric acid.

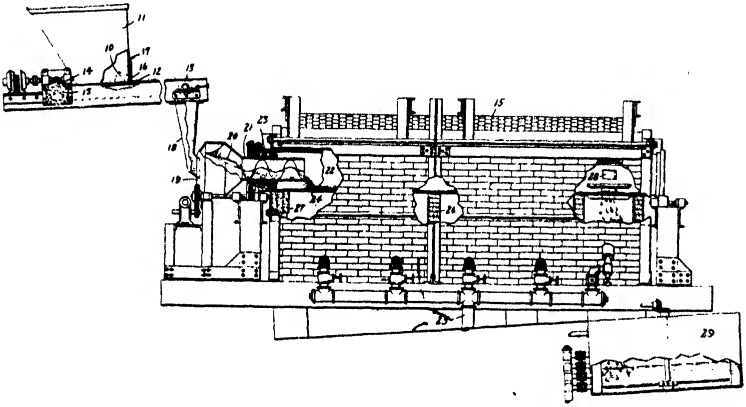


Diagram of apparatus for decomposition of tungsten ore by fusion with sodium carbonate.

As an aid to overall efficiency the mother liquor and wash waters from the settling and washing tank are treated with powdered lime to neutralize the acid and to precipitate calcium tungstate from any tungsten compounds contained in the mother liquor and wash waters.

Gordon and Spring[2] have described in detail the procedure for the manufacture of sodium tungstate and tungstic acid from wolframite by means of the revolving furnace, as illustrated above. The fusion mixture is fed at the rate of 278 pounds per hour, or 140 pounds tungstic acid per hour, and is exposed to the heat about 30 minutes. The fusion as it comes from the furnace contains approximately 55 per cent soluble tungstic oxide. The efficiency of the operation of fusing is 99.35 per cent. The wash water in the lixiviating tank has a specific gravity of 1.70 with suspended sludge at 80°. After filtering, the clear sodium tungstate solution has a specific gravity of 1.47, which corresponds to about 3.5 pounds of tungstic oxide per gallon, and at this concentration is used for the preparation of sodium tungstate crystals. When used for the preparation of tungstic acid, the solution is diluted to a specific gravity of 1.27, or about 2 pounds of tungstic oxide per gallon.

In the manufacture of sodium tungstate crystals the solution is heated to 90° to 100°. This hot, concentrated liquor flows into a receiver, operating under a 20-inch vacuum, which is provided with steam coils to keep the liquor at a temperature from 75 to 85°. The liquor is then discharged into a water-cooled drum, which is rotated at 1 rpm. By cooling the sodium tungstate liquor to 25°, the concentration is reduced to approximately 3.9 pounds of tungstic oxide per gallon by the separation of fine crystals of sodium tungstate. The crystals are separated from the mother liquor by a continuous filter. This process is continued until 70 per cent of the total tungstic oxide has been removed from the solution. The remaining sodium tungstate solution is diluted and used for the precipitation of tungstic acid.

For the manufacture of tungstic acid from sodium tungstate solution, the solution is diluted, as previously stated, to 2.0 pounds of tungstic oxide per gallon, and to it is added a concentrated solution of sodium nitrate in the proportion of 1 pound of sodium nitrate to 25 pounds of tungstic oxide. After being heated to 100°, it flows directly into a precipitating kettle. Tungstic acid is precipitated from the sodium tungstate solution by commercial 20° Bé hydrochloric acid heated to 60°. The earthenware precipitating kettle is set in an oil bath heated by steam coils to 138°. The solution in the kettle is kept in agitation by a steam jet, bringing the temperature of the contents up to 106°. Ninety per cent of the tungstic oxide in the sodium tungstate solution is precipitated as tungstic acid. To decrease the amount of unprecipitated tungstic oxide it is necessary either to raise the temperature of the contents of the kettle or increase the amount of hydrochloric acid. In order to settle the tungstic acid more efficiently, the second wash water is treated with 42° Bé commercial nitric acid. It has been found that aluminum sulfate acts as a coagulant and can be used to good advantage to aid the settling of any colloidal tungstic acid without seriously injuring the purity of the tungstic acid. The tungstic acid is washed six times. The average time of settling for each wash, with the exception of the first, is approximately 10 hours. It has been found that 0.36 per cent of the tungstic acid precipitated is lost in wash waters.

The tungstic acid slurry is dried by means of a rotary drum drier. The drum is operated under a steam pressure of 40 pounds. As tungstic acid is very easily reduced to the blue oxide, it is very important that the enamel coating of the drier be perfect to insure a uniform product. The efficiency of this operation is 98 per cent.

All acid liquors, the first wash water, and other wash waters containing an appreciably amount of tungstic oxide are treated for its recovery. The method of recovering the tungstic oxide is divided into three stages: first, the tungstic oxide in the liquor is converted into calcium tungstate by hydrated lime; second, the calcium tungstate is converted into tungstic acid by the acid liquor, and third, the tungstic acid is converted into sodium tungstate solution by sodium hydroxide. The following equations indicate the reactions taking place during the recovery process:

$$H_2WO_4 + Ca(OH)_2 \text{ in neutral solution} \rightarrow CaWO_4 + 2H_2O$$

$$CaWO_4 + 2HCl \rightarrow \text{crude } H_2WO_4 + CaCl_2$$

$$H_2WO_4 + 2NaOH \rightarrow Na_2WO_4 + 2H_2O$$

According to Smithells[3], by using a rotatory furnace wolframite ore may be treated in the following manner.

The mixture, made up of ore ground to pass a 200-mesh sieve, plus 58 per cent soda ash and 4 per cent sodium nitrate, is charged at the rate of 300 kg per hour to a rotatory furnace, about 15 feet long and 14 inches diameter, which is heated to 980–1000° by gas or oil. The pasty mass containing about 55 per cent soluble tungstic acid gradually falls directly into a tank of water which is allowed to reach a specific gravity of 1.7 at 80° before being emptied. Sodium tungstate is recovered by crystallization after the solution is filtered through cloth. Instead, yellow tungstic acid is precipitated if the liquid is first diluted to a specific gravity of 1.27 and heated to boiling and is then run into boiling hydrochloric acid solution.

The Process of Ludwig Rosenstein and Ernest H. Simonds. U. S. Patent 1,244,082 (1917). This process of extracting trioxide of tungsten is applicable to tungsten ores in general and to scheelite in particular. The scheelite ore to be treated is first finely ground and mixed with about twice its weight of water. Sodium carbonate and sodium hydroxide are then added to the mixture, and the amount of each of the reagents added is determined by the percentage of calcium tungstate present in the ore treated. In practice the percentage of each of the above reagents added must be equal to the percentage of calcium tungstate present in the ore. Five per cent of common salt may be added to coagulate any material that is colloidal, and hence to facilitate subsequent filtration. The mixture is subjected to boiling for 6 hours, during which time soluble sodium tungstate and insoluble calcium carbonate are formed, while sodium hydroxide acts to aid the dissolution. The calcium carbonate precipitated is removed by suitable means, leaving a solution containing sodium tungstate, sodium hydroxide and perhaps an excess of sodium carbonate and salt. The tungstate from this resulting mixture is recovered by adding sufficient amount of slaked lime to react with the excess of sodium carbonate to form calcium carbonate, which is then removed by any convenient means. The liquid mixture is treated with a barium compound in quantity chemically equivalent to the quantity of sodium tungstate present, and this mixture is boiled for 20 or 30 minutes. This results in the formation of barium tungstate and sodium compound. The barium tungstate is transferred into another container and treated with hydrochloric acid. This results in the formation of barium chloride, tungsten trioxide and water. The reason for the intervening step of using a barium compound instead of direct application of hydrochloric acid for the precipitation of tungsten trioxide is that in practice there is always an excess of alkali present which would require an acid consumption so great as to be commercially undesirable; furthermore, direct precipitation of tungsten trioxide with hydrochloric acid would cause the trioxide thus formed to be colloidal and difficult to filter on a large scale.

The Process of Edward M. Hamilton. U. S. Patent 1,261,383 (1918). This process is applicable to treatment of tungsten ores low in WO_3 and containing copper.

The first step of the process is to grind the ore to a suitable fineness, preferably −200 mesh. After this, it is made into pulp with water, and either sodium carbonate or bicarbonate is added to the pulp. The amount of alkali carbonate added is based on the tungsten content of the ore.

With ores low in tungsten, the ratio of alkali to ore is usually kept low, say 1:1 or 2:1. The pulp is heated in an autoclave capable of withstanding high pressure and preferably equipped with an agitator. It is desirable to work this process from one to three hours at 100 lbs of pressure within the autoclave equal to a temperature of 328° F.

Tungsten acid is precipitated in the usual manner by treating the sodium tungstate solution with hydrochloric acid.

Warren F. Bleecker Process. U. S. Patent 1,399,245 (1921). This proposes the use of sulfuric acid to decompose sodium tungstate to tungstic acid. The reaction is best effected by using 60° Baumé sulfuric in the presence of 12 per cent moisture according to the following formula.

$$Na_2WO_4 + 2H_2O + 2H_2SO_4 \rightarrow 2NaHSO_4 + H_2WO_4 + 2H_2O$$

The mass is then heated to expel all the water and to break up the sodium bisulfate, resulting in the formation of tungstic oxide and sodium sulfate according to the following reactions:

$$Na_2WO_4 + 2NaHSO_4 + \text{heat} \rightarrow WO_3 + H_2O + 2Na_2SO_4$$

$$H_2WO_4 + \text{heat} \rightarrow WO_3 + H_2O$$

In order to repress the solution of the tungsten compound entirely, from 0.5 to 1.0 per cent of free hydrochloric acid may be added to the wash water to remove the sodium sulfate and such other salts as may be present in soluble form.

The Autoclave-Soda Process of Maslenitzki.[4] It has been found that soda cannot decompose scheelite completely even with three times the quantity of the theoretical amount required. Improvement is shown when silica is added to the charge, according to the reaction:

$$CaWO_4 + Na_2CO_3 + SiO_2 = Na_2WO_4 + CaSiO_3 + CO_2$$

However, if the ore is low in WO_3 and high in calcite, consumption of soda would be enormous. Experiments have shown that scheelite ground to −200 mesh can be decomposed completely by a solution of soda, heated to 190–200° in an autoclave at a pressure of 15 atmospheres, according to the formula

$$CaWO_4 + Na_2CO_3 \rightarrow Na_2WO_4 + CaCO_3$$

The amount of soda required for rich concentrate is approximately three times the WO_3 content in the ore by weight, while for poor concentrates, the amount is 4 to 4½ times.

The Autoclave-Soda Process of Robert G. Hall: U. S. Patent 2,351,678 (1944). The pulp ratio employed in the autoclave is three parts of water to one part of scheelite, of suitable mesh screen, added to which is sodium carbonate in amount of 2 parts or more Na_2CO_3 to 1 part WO_3 by weight. The autoclave is maintained at a temperature of 380° to 390° F under a pressure of about 200 lbs per sq in. The actual time required for complete reaction of the calcium tungstate to sodium tungstate is from 2½ to 4 hours. For the neutralization of any excessive sodium carbonate still remaining, sulfuric acid is employed according to the formula

$$H_2SO_4 + Na_2WO_4 + Na_2CO_3 = Na_2SO_4 + H_2O + CO_2 + Na_2WO_4$$

For the precipitation of the tungsten as tungstate of iron, ferrous sulfate is employed, according to the formula

$$Na_2WO_4 + FeSO_4 = FeWO_4 + Na_2SO_4$$

from which the $FeWO_4$ is filtered out and washed. If it is cleaned to obtain the product in the form of WO_3 it is only necessary to treat the $FeWO_4$ with sulfuric acid whereby ferrous sulfate is recovered for reuse in the above step and tungstic acid (H_2WO_4) remains as an insoluble residue. By drying and heating the H_2WO_4, the tungstic oxide WO_3 is obtained.

Practical application of the autoclave-soda process has been carried out by the U. S. Vanadium Corporation with low-grade scheelite concentrates, as already described in Chapter III. Instead of using an autoclave, the plant of the Golconda Division of the Nevada-Massachusetts Co. adopts the Dwight-Lloyd sintering machine for the treatment of low-grade tungsten concentrates with soda. The flowsheet* on page 168 shows the treatment of this peculiar ore. It is supposed that the tungsten occurs as a colloid in the iron-manganese minerals of the ore.

In the old methods as described by Scheibler[5], Bernoulli[6] and Zettnow[7], soda ash was generally used to decompose the ore and the smelting was carried out in crucibles. Bucholz[8] proposed the use of potassium carbonate for fusion with the wolframite in the ratio of 2 to 1 in weight.

I. 2. Decomposition with sodium nitrate

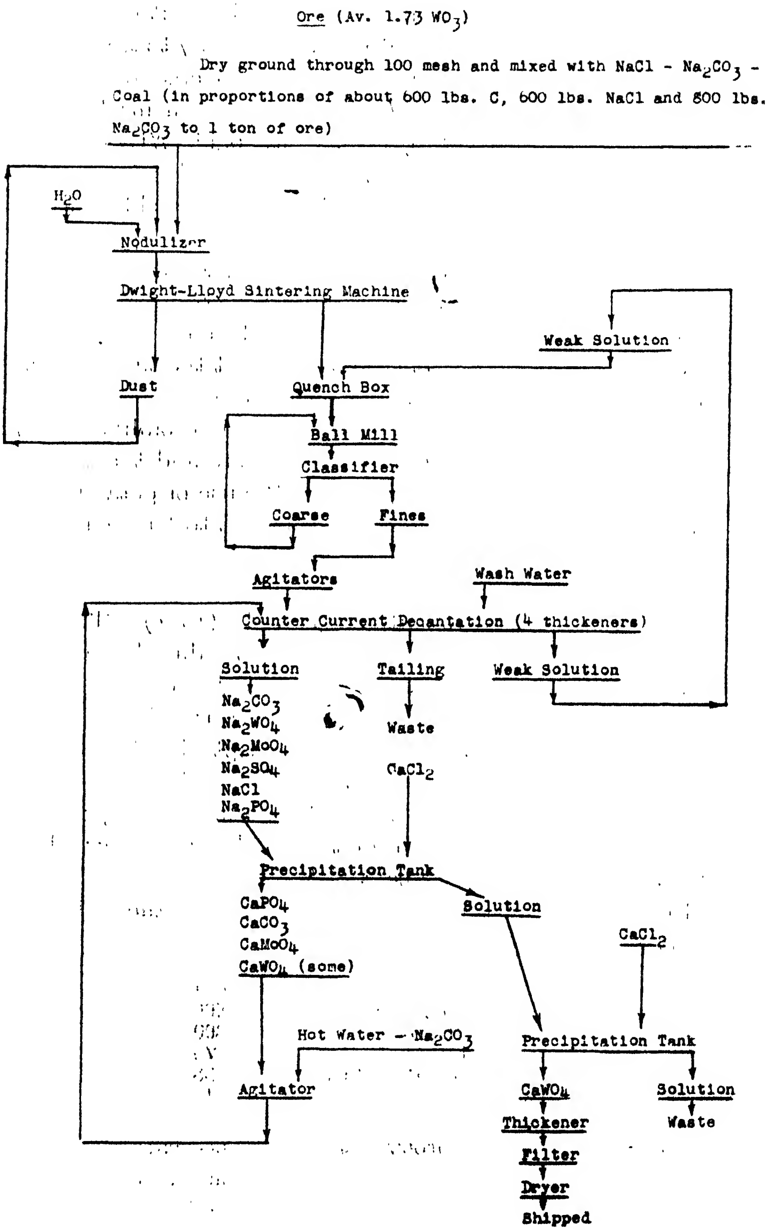
William B. Stoddard. U. S. Patent 1,652,646 (1927). The tungsten-bearing ore as well as the charcoal used are first reduced to powder. To this mixture water and sodium silicate are added and are thoroughly incorporated. Finally, powdered sodium nitrate is added. The whole mixture is then placed into a shallow, open receptacle; it is then ignited, whereupon the combustion will propagate itself completely throughout the mass. Upon the completion of the operation, the resulting soluble tungstate is separated by lixiviation from the residue in the usual manner. Recovery is as high as 98.97 per cent of the tungsten content in the ore treated. In carrying out this process, a mixture of the following composition may serve as an example:

	Parts
Tungsten-bearing ore	500
Sodium nitrate	300
Charcoal	75
Sodium silicate solution	38
Water	13

It is to be noted that, in this process, the heat necessary to effect the required chemical changes results from the interaction of the oxygen of the sodium nitrate with the charcoal and that the combustion of the carbon

---

* Information from Mr. S. P. Warren and Mr. Charles H. Segerstrom.
Vide: Huttl, John B., "Unique Golconda Deposit Yields Its Tungsten," *Eng. Min. J.*, 79–81 (Aug., 1945).



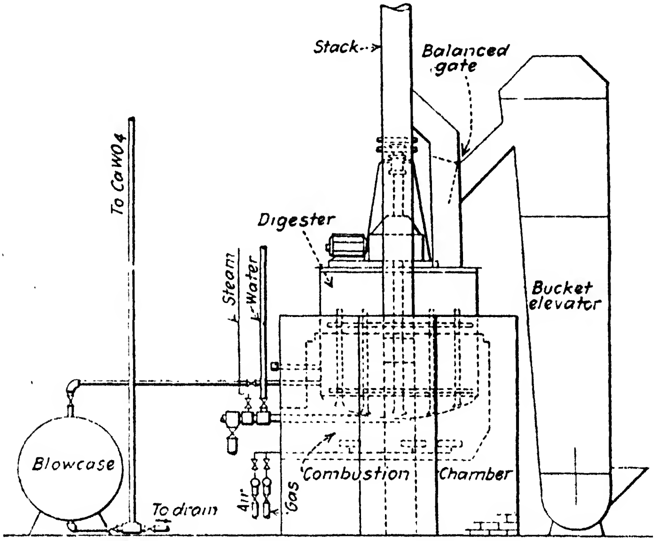
Flowsheet showing treatment of low-grade scheelite concentrates.

by the oxygen of the sodium nitrate will produce nascent sodium carbonate, which in turn reacts with the tungsten ore, forming the soluble tungstate.

Compagnie Française pour l'exploitation des procédés Thomson-Houston. French Patent 591,586 (1924). According to this patent only sodium nitrate is used: to every 4 kg wolframite (60 per cent WO_3) 2 kg of sodium nitrate is added, together with a little water.

I. 3. Decomposition with alkali hydroxide

A digester[9], as illustrated below, is employed. First the required quantity of water is added to the digester, the agitator started and the necessary caustic soda charged. Heat is then applied and, as soon as the caustic soda is in solution, the calculated quantity of wolframite ore is added. Steam is applied to prevent the ore from settling on the bottom. After decomposition is complete, water is added to give a definite volume and the gangue is allowed to settle. The clear sodium-tungstate solution is then decanted into a blowcase. The residue in the digester is leached with water until free of soluble tungstates and the leachings added to the strong sodium tungstate solution.



Equipment for digestion of wolframite ore.

G. A. Hempel. German Patent 221,062 (1907). A cleaner tungstate is obtained when a small percentage of caustic lime is added to the caustic alkali used to treat wolframite ore in an autoclave. Apparently under a pressure of 6 atmospheres and at 180°, the calcium would form insoluble compounds with such impurities as silica, tin, etc.

D. J. Giles and J. E. Giles. U. S. Patent 1,293,403 (1919). The tungsten ore, either wolframite or scheelite, is treated with the calculated amount of sodium hydroxide (NaOH) in a closed vessel, to which heat is applied. The steam thus produced gives a pressure of about 60 lbs per square inch in the apparatus. In the reaction taking place in the closed vessel, some silica and phosphorus are attacked by the sodium hydroxide, forming solutions of sodium phosphate and sodium silicate. The removal of phosphorus and silica is accomplished by treating the solution coming from the autoclave at room temperature by diluting to almost about 0.8 per cent sodium hydroxide and adding calcium hydroxide in excess, according to the following equations:

$$Ca(OH)_2 + Na_2SiO_3 \rightarrow CaSiO_3 + 2NaOH$$

$$3Ca(OH)_2 + 2Na_3PO_4 \rightarrow Ca(PO_4)_2 + 6NaOH$$

These insoluble compounds are filtered off and the filtrate is treated with milk of lime at 200° F according to the formula

$$Ca(OH)_2 + Na_2WO_4 \rightarrow CaWO_4 + 2NaOH$$

The precipitated $CaWO_4$ is separated from the liquid by decantation or filtration, and is treated with hydrochloric acid. The reaction is as follows:

$$CaWO_4 + 2HCl \rightarrow H_2WO_4 + CaCl_2$$

This process may be quite economical because all the reagents used can be recovered.

C. V. Iredell. U. S. Patent 1,796,026 (1931). It has been found that when the caustic mother liquors resulting from the crystallization of the alkali tungstates are treated for the recovery of the tungsten contained either with hydrochloric acid or with calcium chloride, the products obtained are impure, because of the presence of calcium oxides or hydroxides in the case of calcium chloride; also, relatively high losses of tungsten as soluble or colloidal particles are experienced when hydrochloric acid is used. The following method of treatment has been found to obviate all these difficulties.

To the mother liquor a solution of dilute hydrochloric acid is added, slowly and with constant stirring until an alkalinity of from 0.3 to 0.7 per cent is obtained with phenolphthalein as indicator. At an alkalinity lower than 0.3 per cent the tungsten is incompletely precipitated from the solution as calcium tungstate. At an alkalinity higher than 0.7 per cent, a slowly settling, bulky precipitate containing large amounts of occluded impurities and associated calcium oxide is obtained, which is exceedingly difficult to filter and to wash. When calcium salt such as the chloride or nitrate is used, the resultant calcium tungstate precipitate is crystalline and not amorphous as is usually obtained; it has the formula $CaWO_4 \cdot H_2O$. Before the above treatment the mother liquor is diluted until a sodium tungstate content of approximately 120 to 150 grams per liter is obtained.

F. M. Becket. U. S. Patent 1,431,559 (1922). In the treatment of tinny wolframite ore with caustic soda, a roasting operation is necessary. The fine ore, preferably 40 mesh and finer, is first subjected to an oxidizing roast at a temperature of about 460 to 720°. Lower temperatures down to 300° give somewhat inferior-results, while higher temperatures up to 900° render the tungsten content of the ore substantially insoluble.

I. 4. Decomposition with ammonia

F. W. Wilder, E. Morris, E. Schiff, E. S. King. British Patent 291,919 (1928). A solution of ammonia gas in water with or without the addition of ammonium carbonate or other ammonium salt is used to treat, under elevated pressure, complex ores or residues containing tungsten. By concentrating the resulting solution the paratungstate crystallizes out. The same method of treatment is contained in Austrian Patent No. 12736, 1928.

I. 5. Decomposition with fused alkali

C. H. Fischer. British Patent 17,603 (1912). For the treatment of scheelite ore it is proposed to use a large excess of fused caustic alkali to which is mixed a small quantity of lime. The fusing mixture may be made up thus:

	Parts
Caustic potash	400
Burnt lime	30
Ground scheelite ore	200

The purpose of the lime is to prevent the formation of silicic acid. The cooled mass is then ground and lixiviated in water to dissolve out the potassium tungstate and leave the impurities.

C. C. Buré. French Patent 522,682 (1920). Wolfram ore is treated with sodium hydroxide under fusion. Sodium tungstate is then obtained by lixiviating the fused product with water.

I. 6. Decomposition with bisulfate

J. J. Berzelius[10] first attempted to use sodium bisulfate ($NaHSO_4$) for the decomposition of wolframite ore. L. Weiss and A. Martin[11] showed that the use of potassium bisulfate ($KHSO_4$) for the decomposition of wolframite ore gives poorer results than soda.

E. F. J. Clotten. German Patent 141,811 (1902). The procedure for carrying out the process is as follows: First ignite the ore alone with

$NaHSO_4$, up to 300°, then add a mixture of the bisulfate and lime or calcium chloride, with an addition of alkali chloride and gradually raise the temperature to 800°. The final product of sodium tungstate is treated in the usual way.

The Bisulfate Process of the Kempen Electrochemical Factory. German Patent 149,556 (1902). Sodium bisulfate is heated with mono-hydrated sulfuric acid, and when fusion has commenced the finely pulverized wolframite is introduced. The solution obtained by lixiviation contains the tungsten as sodium acid tungstate while some of the foreign matter is present as sulfates. The latter may be precipitated by electrolysis. Upon evaporating the residual solution, sodium sulfate is deposited and the tungstic acid is precipitated by the addition of hydrochloric acid.

Gin's Modification of the bisulfate process[12]**.** Alkali bisulfate is fused first before the finely pulverized wolframite is thrown in. "The mass, after solidification, is broken up, finely pulverized and treated with water which dissolves soluble sulfates of the metals and phosphoric acid and leaves insoluble potassium acid tungstate as a white amorphous mass. The insolubility of the acid tungstate is true only of acid solutions which necessitates the use of an excess of bisulfate above that indicated by the following reaction.

$$5Fe_3MnW_4O_{10} + 24KHSO_4 + 4H_2O \rightarrow$$

$$\underbrace{4(2K_2O\cdot 5WO_3\cdot 4H_2O)}_{\textit{Insoluble}} + \underbrace{15FeSO_4 + 5MnSO_4 + 4K_2SO_4}_{\textit{Soluble}}$$

"In practice, about 50 per cent excess of bisulfate is used so as to insure complete attack, supply loss, and keep in the solution sufficient acid to insure the insolubility of the tungstate, while at the same time it insures the solution of any phosphates which may be present.

"The insoluble residue after separation from the acid solution consists not only of tungstic acid, but also of silica, cassiterite and insoluble sulfates. It is dried and treated at 40° with warm water containing some ammonium carbonate, or cold water may be used, to which is added ammonia, and a current of carbonic acid passed through. Under these conditions, the acid tungstate dissolves, while the silica and cassiterite remain insoluble:

$$2K_2O\cdot 5WO_3\cdot 4H_2O + 5(NH_4)_2CO_3 \rightarrow 2K_2CO_3 + 5(NH_4)_2WO_4 + 3CO_2 + 4H_2O$$

"In reality, the neutral ammonium tungstate is not obtained, but on evaporation of the solution paratungstate is produced, while the ammonia in excess escapes until a salt of the following composition results: $5(NH_4)_2$

$O \cdot 12WO_3 + nH_2O$, in which n varies from 11 to 5 according to the temperature of evaporation. The salt obtained crystallizes in plates or in acicular forms; it loses water of crystallization at 100°; when heated in contact with the air it is decomposed, leaving tungstic acid containing a little nitrogen which causes no inconvenience in metallurgical work, for the nitrate and the oxy-nitride are both decomposed above 1,200°."

I. 7. Decomposition with calcium carbonate and sodium chloride

F. Jean[13] and L. Weiss[14] and A. Martin recommended the use of lime or calcium carbonate with the addition of sodium chloride for the decomposition of wolframite ore. It was observed that the addition of sodium chloride was absolutely necessary. According to L. Weiss the charge may be made up thus: 200 parts wolframite, 200 parts powdered marble or 200 parts wolframite, 50 to 100 parts calcium chloride.

Using the same method, Alfred C. Wu[15] obtained the following results:

(a) Heating the ore with 25 to 30 per cent calcium carbonate and 25 per cent sodium chloride.

(b) Heating at 700 to 775°.

(c) Heating for 30 minutes to 2 hours.

It was observed that upon heating the charge, both the amount of calcium carbonate present and the time of heating have profound influences on the extent of rendering wolframite acid-soluble. For every increase of 5 per cent of the weight of the ore in the amount of calcium carbonate used, the extraction of tungstic acid is increased approximately 9 per cent. Increasing the time of heating at 700° to 2 hours gives better yield than raising the temperature to 775°. This procedure gives 95 per cent extraction.

I. 8. Decomposition with neutral salts. Process of F. Jean[16].

Wolframite ore, ground to a very fine powder, is mixed with 20 to 30 per cent of sodium chloride and 3 per cent of calcium carbonate, and heated for a half hour in a crucible in a reverberatory furnace. The reaction is as follows:

$$Fe_3MnW_4O_{16} + 8NaCl \rightarrow Na_2WO_4 + 3FeCl_2 + MnCl_2$$

Upon cooling, the mass is pulverized, boiled with HCl to dissolve the lime and the oxides of iron and manganese, disengaging chlorine, and leaving all the tungstic oxide as an insoluble lemon-yellow powder. This process may be applicable only to very pure wolframite, for silica, if present, is not attacked by sodium chloride.

Process of Gin[17]. A mixture of finely pulverized wolframite with magnesium chloride is heated in a reverberatory furnace at a temperature of

1,200 to 1,300°. "There are formed magnesium tungstate and a certain proportion of chlorides of iron and manganese which almost entirely distill off. On continuing to heat with an oxidizing flame the iron remains as a peroxide. The mass is cooled, pulverized, treated with a small quantity of cold water to dissolve the chlorides and to leave undissolved the crystals of magnesium tungstate. The residue is then taken up in boiling water, the oxides of iron and manganese remain insoluble, likewise silica. The tungstic acid is in solution as magnesium tungstate which crystallizes after concentration as vitreous tufted prisms of the formula $MgWO_4 \cdot 7H_2O$.

"Some silica will remain in solution as silica-tungstate. The mother liquor is decanted, wash water added to it, and it is then treated with ammonium carbonate to precipitate the magnesia and keep the tungstic acid in solution. On evaporating, ammonium tungstate is obtained, which is decomposed by calcination."

The Sodium Sulfate Method[18]. Fusion of wolframite with sodium sulfate alone results in very poor yields. Better results are obtained if powdered coke is added. The reaction which takes place is represented by the equation:

$$FeWO_4 + 2Na_2SO_4 + 2C \rightarrow Na_2O + 2SO_2 + 2CO + FeO + Na_2WO_4$$

A mixture of the following composition gives comparatively good results: 30 per cent salt-cake (commercial sodium sulfate), 10 per cent sodium carbonate and 10 per cent powdered coke, fused with the wolframite at 665°.

The Potassium Sulfate Method[18a]. Fusion of wolframite with or without magnesia and sodium chloride has been tried but the results were very poor.

J. C. Blanch. German Patent 330,987 (1920). The ore is roasted with sodium chloride and then with an admixture of a nitrate. The roasted product is treated with sulfuric acid and agitated with steam. The resulting tungstic oxide is finally washed.

S. J. Lubowsky. U. S. Patent 1,410,584 (1922). The ore is roasted with calcium chloride, sodium chloride or potassium chlorate at a temperature of about 1,700° F. The roasted product, after being pulverized, is treated with a fairly concentrated mineral acid, such as sulfuric, nitric, or hydrochloric. As a result of this treatment a large percentage of the original impurities of the ore goes into solution. The solid residue is then washed and treated with ammoniacal liquor or a solution of ammonium carbonate at about 40°. The resulting solution is then separated and the ammonia is distilled off and recovered by any well-known method. The residue remaining is tungsten trioxide.

Decomposition with Alkali Fluoride. This method is applicable to the treatment of scheelite. The ore is fused with potassium fluoride in a reverberatory furnace. The resulting products are alkaline tungstate and calcium fluoride; the latter, being insoluble, can be easily separated out.

I. 9. Decomposition with Acids

C. M. Johnson. U. S. Patent 946,870 (1910). Charge a quantity of wolframite or scheelite in a vitrified clay kettle, together with a chlorine-affording substance (sodium chlorate or potassium chlorate) in small amount, 1 part of chlorate to 100 parts of ore. Add to this charge hydrochloric acid in the ratio of 125 to 150 pounds of ore to 111 pounds of 20° acid. Maintain the temperature in the kettle at about 90°. The reaction requires 10 to 18 hours. Decant the solution and wash the residue with water thoroughly to get rid of all solubles. The residue consists of tungstic acid and silica dross. Soluble tungstate is obtained by treating the residue with ammonia water in the usual manner. Or, the residue may be employed direct for the manufacture of tungsten steel.

J. Ban. U. S. Patent 1,049,193 (1912). Finely powdered wolframite is heated gently with strong hydrochloric acid. After reaction the solution is allowed to cool. Then the clear solution is poured away and the residue thoroughly washed with clear water. The residue is then treated with a concentrated solution of bleaching powder, to which a suitable quantity of hydrochloric acid is added, and stirred up slowly. It will be observed that by this agitation the calcium hypochlorite, acted upon by the hydrochloric acid, will liberate chlorine in the nascent state, which will make soluble any iron, manganese, or other substances still existing in the residue. A solution of citric acid is added to the liquor to convert any insoluble chloride of diabase iron that may be formed into a soluble citrate of iron. The remaining residue, after being thoroughly washed with water, is treated with ammonia in the usual manner for the formation of ammonium paratungstate.

J. C. Butterfield. British Patent 10,117 (1915); U. S. Patent 1,217,914 (1917). The wolframite ore is first treated with dilute sulfuric acid, under boiling, to dissolve out a portion of the iron and manganese contents of the ore. The residue is again treated with sulfuric acid, sodium chloride and sodium nitrate to complete the removal of the iron and manganese oxides. By this treatment the residue is exposed to the extractive action of hydrochloric acid *in statu nascendi* evolved by the action of sulfuric acid upon the sodium chloride, as well as subjected to the action of chloro-nitric gas evolved from the nitrate and chloride by the sulfuric acid. The residue obtained after the above treatment consists of tungstic acid or oxide.

K. Anjow. U. S. Patent 1,483,567 (1924); British Patent 241,399 (1925). It is well known that wolframite or scheelite is difficultly and only slightly acted upon by dilute sulfuric, hydrochloric, or nitric acid, and that even when the ore is treated with concentrated sulfuric, hydrochloric or nitric acid at its boiling temperature the decomposition of the ore into WO_3 is incomplete. According to Anjow, a coating or film is formed on the surface of the ore when the latter is acted upon by the acid, and it is this coating that prevents the further action of the acid upon the ore. The coating or film consists chiefly of sulfates, chlorides or nitrates of iron, manganese, calcium and other metallic impurities, which although soluble in dilute acid, are only sparingly so in the concentrated one. In order to obviate the above drawbacks the ore is finely pulverized and is treated under pressure in an autoclave fitted with a stirrer at a moderate temperature.

Three parts of 10 per cent (by volume) sulfuric acid and one part of powdered wolframite (1/70 mm or finer) are put in an autoclave, which is provided with a stirrer. While stirring, it is heated to 180° under pressure, by which treatment the iron and manganese in the ore are completely converted into soluble sulfates. After half an hour of treatment, the mixture is removed into a settling tank, and the clear solution is then decanted off, leaving the residue of tungstic oxide behind.

Either hydrochloric acid or sulfuric acid can be employed to decompose scheelite, although the usual practice is to use the former. With the use or hydrochloric acid, the procedure is as follows: Four parts of 18 per cent hydrochloric acid and one part of powdered scheelite (1/50 mm or finer) are put in a tank provided with a stirrer and an acid-proof lining; while stirring it is heated by steam or direct firing to 80° for one hour. by which treatment calcium in the ore is converted into chloride while tungstic oxide is formed. When sulfuric acid is used, the procedure is as follows: Three parts of 15 per cent (by volume) sulfuric acid and one part of the powdered scheelite (1/200 mm or finer) are charged in an autoclave having a stirrer and an acid proof lining; while stirring it is heated by steam or direct firing to 150° under pressure, by which treatment calcium and other impurities are converted into sulfates while tungsten oxide is formed.

Arthur W. Hixson. U. S. Patent 2,261,371 (1944). Tungsten ore, containing either manganese or iron or both, is finely ground and suspended in water. Sulfur dioxide gas is then bubbled through the water with the ore in suspension. By this operation both the tungsten and manganese of the tungsten-manganese ore go into solution while both the tungsten and iron of the tungsten-iron ore remain as such in the residue after filtration. The clear solution containing tungsten and manganese is boiled, with evolution of sulfur dioxide, which is then returned to the first step in the process. Simultaneously a white precipitate is deposited which contains nearly all the tungsten that was in solution. This impure precipitate can be purified by being digested with nitric acid, causing the formation of a pure yellow tungstic acid which is filtered off leaving the nitric acid solution for further use. The solid residue from the first part of the process, containing the tungsten and iron, is then suspended in water at 40° to 100°, and treated with a gaseous mixture of sulfur dioxide and air. Under these special conditions the iron dissolves, leaving behind a residue of tungstic acid and silica. After filtration, the residue is treated with an ammonium hydroxide solution when the tungstic acid dissolves. On evaporation, ammonium paratungstite is formed. The salt is roasted, forming solid tungstic acid while ammonia goes off as a gas, to be absorbed in water for reuse.

Decomposition of scheelite by hydrochloric acid, according to C. J. Smithells.[20] Into a steam-heated, rubber-lined vessel of iron or earthenware, fitted with mechanical stirrers, are put 180 liters of commercial hydrochloric acid, and to this 150 kg of scheelite, ground to pass 120 mesh, is added. The reaction is represented by the equation $CaWO_4 + 2HCl \rightarrow WO_3 + CaCl_2 + H_2O$. The temperature is raised to 70° during 2 hours, and maintained for a further 5 hours. In order to oxidize the impurities, about 300 cc of nitric acid are added. After the liquid is syphoned off, the sludge is washed four or five times by decantation with boiling water. To prevent the tungstic acid from becoming colloidal, 5 per cent of hydrochloric acid is added to the third wash water.

I. 10. Separation as Chloride

Tungsten forms a series of volatile chlorides and oxychlorides when heated with chlorine, hydrochloric acid gas, carbon tetrachloride or sulfur chloride. The most important of these compounds are tungsten hexachloride (WCl_6), tungsten oxytetrachloride ($WOCl_4$) and tungsten dioxydichloride (WO_2Cl_2). The lower chlorides such as the di-, tri-, tetra- and pentachlorides are formed from the reduction of hexachloride. The two oxychlorides, WO_2Cl_2 and $WOCl_4$, are volatile below 300°, while the chloride WCl_6 is volatile at a somewhat higher temperature. Many processes have been suggested for the separation of tungsten, as chlorides, from its ores, but they are not in general economical. They may be practicable in the treatment of low-grade ores or ores containing tin.

(a) **Treatment with chlorine or hydrochloric acid gas: W. H. Dyson.** British Patent 176,428 (1922); British Patent 179,201 (1922); U. S. Patent 1,481,697 (1924). The crushed ore—either wolframite or scheelite containing tin as impurity—is agitated in a furnace provided with an acid-proof lining at a temperature of 600°. A mixture composed of equal volumes of chlorine and hydrochloric acid gas is then led over the heated ore, resulting in the complete volatilization of the tin, together with 1–2 per cent of the tungsten. The temperature of the furnace is then raised to 1000° while the gaseous mixture is passed over the residue, with the result that the iron, manganese and tungsten are volatilized as chlorides. These vapors are led into water, whereby the iron and manganese go into solution while the tungsten is precipitated as tungstic acid.

O. J. Stannard. British Patent 134,891 (1919). In this process the crushed ore is mixed with a certain percentage of carbonaceous material, such as coke, and heated to 300° in a current of dry chlorine. By this means the tungsten volatilizes as chlorides or oxy-chlorides along with the iron and manganese. Treatment with acidified boiling water precipitates the tungsten acid, and the chlorides of iron and manganese are recovered by evaporation.

(b) **Treatment with carbon tetrachloride: P. Jannasch.** German Patent 266,973 (1910). It is known that when carbon tetrachloride is passed over tungstic oxide heated to redness the following reaction takes place:

$$WO_3 + CCl_4 \rightarrow WOCl_4 + CO_2$$

$$2WO_3 + CCl_4 \rightarrow 2WO_2Cl_2 + CO_2$$

In the treatment of wolframite ore with carbon tetrachloride, however, it is necessary to mix intimately the pulverized ore with a large quantity of quartz, pure sand or silica. The tungsten chloride or oxychloride, resulting from this treatment, is treated in the usual manner, as indicated above.

(c) **Treatment with sulfur chloride and chlorine: L. G. Jeness.** U. S. Patents 1,834,622 (1931); 1,863,599 (1932); 1,923,094 (1933). The pulverized ore, of about 100 mesh in size, is first roasted in a furnace for from two to three hours at about 700°. The object of this preliminary roasting is to cause a cracked or porous condition of the ore particles, thus providing more surface on which the gases may act.

After this roasting treatment, sulfur dichloride (SCl_2) and chlorine (Cl_2) are passed over the ore while a temperature of about 200° is maintained in the furnace. At this temperature a compound of tungsten is formed which is soluble in aqueous solution but which is not volatilized at that temperature. The residue can then be treated with sodium carbonate or ammonium hydroxide to form the sodium tungstate or ammonium paratungstate.

M. L. Ross. U. S. Patent 2,077,073 (1937). The ore is first ground to a fineness of 200 mesh. It is then digested with sulfur chloride (a mixture of S_2Cl_2 and SCl_2) at a temperature within the range 125 to 138°. The proportion of ore to sulfur chloride used is 50 parts to 125 parts by weight, respectively. This treatment may be carried out for periods of from 4 to

7 hours in an atmosphere of chlorine. Further treatment of the mass by water results in the formation of tungstic acid, which is converted into ammonium paratungstate by treatment with ammonium hydroxide.

I. 11. Decomposition by Electrolysis

R. E. Pearson, E. N. Craig and Durelco, Ltd. British Patent 185,842 1922). The present method for the production of sodium tungstate from wolframite by means of electrolytic treatment has not been developed industrially. Either an acid or an alkaline electrolyte may be employed. In the former case the tungstic acid formed is insoluble in the electrolyte, whereas the oxides of metals (such as iron, manganese and tin) are soluble in the electrolyte. In the latter case, it is the tungstic acid which is soluble in the electrolyte, whereas the oxides of the contaminating metals are insoluble. The wolframite ore is ground and mixed to a paste with sulfuric acid and the mixture is placed on a lead plate which forms the anode of an electrolytic cell containing dilute sulfuric acid. On passing a current through the cell the iron, manganese, tin, calcium or sodium oxides pass into solution, leaving a residue of tungsten oxide. When a caustic soda solution is used as the electrolyte, the sodium tungstate formed goes into solution, while the iron and manganese are converted into the insoluble oxides Fe_2O_3 and Mn_3O_4.

I. 12. Decomposition by Volatilization

Metallwerk Plansee. British Patent 269,947 (1928); German Patent 480,287 (1929). It is proposed to roast the ore in two stages. At the lower temperature the ore is completely desulfurized, then at about 1000° the iron-manganese-tungsten compounds are decomposed, when the WO_3 is volatilized and is caught in a condenser. Practical application of this method does not seem likely.

Paul Schwarzkopf. U. S. Patent 1,800,758 (1931). By the process of volatilization tungsten products can be obtained free from molybdenum. Tungsten ores are first subjected to the reducing action of carbon or hydrogen and then heated progressively when at about 800° molybdenum is volatilized off first as MO_3 and then finally at 1200–1300° tungsten trioxide vapour WO_3 is formed and is collected in suitable condensation chambers.

I. 13. As sulfide[21].

The decomposition of the ore by means of alkali sulfide or a mixture of carbon and glauber salt can be carried out in a reverberatory furnace. Tungsten, together with tin, molybdenum, arsenic, antimony, iron and a part of copper will dissolve in the melt, while bismuth, lead and copper remain as sulfides in the residue. Upon adding ammonium chloride and an excess of H_2SO_4 to the solution, a light brown deposit of WS_3 is obtained.

I. 14. With Hydrogen Sulfide.

When scheelite and powellite are treated with sodium carbonate and carbon under suitable conditions, both sodium tungstate and sodium molybdate are formed. By passing SO_2 gas into the solution, *unstable* complex salts of tungsten are formed while probably sodium thiomolybdate (Na_2MoS_4) may be formed. However, if H_2S is used, instead of SO_2, both sodium thiotungstate (Na_2WS_4) and sodium thiomolybdate (Na_2MoS_4) are formed; the former is exceedingly soluble in water while the latter may not be so. Further the insoluble thiomolybdate can be formed by adding a solution of the sodium thiomolybdate to a solution of the metal salt[21a]; or molybdenum can be separated out by heating to about 550° the thiomolybdate solution with powdered zirconiumin in a vacuum[21b].

II. PURIFICATION OF TUNGSTIC OXIDE

The tungstic acid, oxide or tungstate prepared by any of the processes described is always impure and requires further treatment for its purification. The nature of the impurities depends on the composition of the ore, on the materials employed and on the type of process adopted. The usual impurities present are iron, manganese, calcium, molybdenum, alumina and silica. Certain ores contain traces and sometimes significant percentages of lead, copper, titanium, sulfur, phosphorus, arsenic, antimony, bismuth, copper and tin. Fortunately some of these impurities are largely eliminated during processing in the manufacture of tungsten salts. Some of the impurities in the ore, such as calcium, silica, arsenic and phosphorus, have an adverse effect upon the amount of tungsten recovered. Extreme chemical purity is required of the oxide for the manufacture of the metal, especially filament; tungstic acid having a maximum of 0.05 per cent impurities, will be acceptable only for the manufacture of metallic tungsten. Tungsten containing 0.1 per cent of iron, for example, is almost unworkable for ductile tungsten because of its brittleness. It is comparatively easy to reduce the total impurities to 0.1–0.5 per cent, but elaborate processes are required to reduce them to 0.05 per cent.

II. 1. Precipitation as Tungstic Acid

Both the color and the state of subdivision of the tungsten oxide produced are conditioned by the following factors:

(a) Concentration of the solutions.
(b) Nature of the acid.

(c) Temperature.
(d) Manner of bringing the solutions together.
(e) Amount of agitation.

This subject has been studied by L. Moser and J. Ehrlich[22]. Best results are obtained by running the tungstate solution into the boiling acid. Upon rapid mixing, coarse-grained precipitate is obtained. If cold hydrochloric acid of specific gravity 1.19 is added slowly dropwise to the cold solution of tungstate, the precipitate first formed passes into the colloidal state upon the addition of more acid, and eventually the colloid is coagulated on boiling. If nitric acid is used, the precipitate does not pass into the colloidal state. The washed precipitate as obtained by hydrochloric acid is fairly soluble in nitric acid, whereas the precipitate produced by nitric acid is scarcely soluble in hydrochloric acid. Sulfuric acid stands midway between hydrochloric and nitric acids in that the precipitate first formed is only partly redissolved upon the addition of more acid. As the colloidal condition tends to favor the absorption of impurities, it is essential to avoid it. In general, the use of cold, dilute solutions tends to favor the production of colloidal precipitates; these are almost white, whereas the coarse hydrated oxide is deep yellow.

The precipitated oxide invariably carries down with it some of the salts dissolved in the solution. For example, if the solution of ammonium tungstate containing 0.2 per cent of iron is run into boiling hydrochloric acid, the precipitated tungstic acid may contain 0.05 per cent of ferric chloride; and when precipitated from sodium tungstate the tungstic acid contains 0.1 to 0.3 per cent of sodium chloride. Repeated washing may to some extent remove the soluble impurities; but this operation tends to render the tungstic acid colloidal, so that it is difficult to filter the solution. To partially obviate the peptization of the tungstic acid, 10 per cent hydrochloric or nitric acid or ammonium chloride is added to the wash water.

II. 2. Crystallization as Ammonium Tungstate

The most practical method of purifying the sodium tungstate obtained by the processes described is to transform it to ammonium paratungstate.

According to Smith and Exner[23a], the ammonium tungstate is digested with nitric acid (1:1) and a little hydrochloric acid giving rise, with thorough washing, to tungsten trioxide, which, upon dissolving in ammonia, crystallizes out again as paratungstate. Upon repeating the process several times pure paratungstate is obtained. This salt, on further digesting with nitric acid and a little hydrochloric acid, yields pure tungsten trioxide upon evaporating to dryness. A recent procedure of this method is thus summarized by C. J. Smithells[23].

"Precipitated tungstic acid dissolves readily in ammonia provided it has not been dehydrated by drying at too high a temperature. Tungstic acid dried at 170° contains 7–8 per cent water, and has practically the theoretical composition H_2WO_4. Dried at higher temperatures it loses water and becomes less soluble, and if ignited above 500° becomes practically insoluble in ammonia, although it can still be dissolved in sodium or potassium hydroxide. Solutions of tungstic acid in ammonia are unstable, and on standing, crystals of hydrated ammonium paratungstate, having the general formula $5(NH_4)_2O \cdot 12WO_3 \cdot xH_2O$, separate out. The degree of hydration, and the crystalline form, depend upon the temperature at which the solution is held during crystallization. If the salt is allowed to crystallize from the solution at room temperature, fine white needles of the composition $5(NH_4)_2O \cdot 12WO_3 \cdot 11H_2O$ are formed. These are converted by prolonged boiling with water into transparent plates, having the composition $5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$, which may also be prepared by direct crystallization from the boiling solution. Both salts are insoluble in either hot or cold water. The paratungstate plates are most conveniently prepared by evaporating the solution rapidly. The decomposition of, 150 kg of scheelite produces a paste containing about 100 kg of WO_3 and this is dissolved in 100 litres of water. The tungstic acid goes into solution very readily, leaving a white residue of lime and silica. After settling, the solution of ammonium tungstate is syphoned into storage vats and, to prevent immediate separation of insoluble ammonium paratungstate, it is diluted to a specific gravity of 1.12. This solution is evaporated to about one-fifth of its bulk in steam-heated enamelled iron pans, the white crystals of ammonium paratungstate being removed as evaporation proceeds, washed on a filter with cold water and finally dried on wooden trays. A yield of about 100 kg. of pure crystals is obtained. The iron which is present in the original solution becomes concentrated in the mother liquor, and imparts to it a deep amber colour. If the crystallization is carried too far the crystals become discoloured, and even when apparently white may contain up to 0.05 per cent Fe_2O_3.

"Paratungstate needles are prepared by dissolving the tungstic acid in excess of ammonia, carefully neutralizing the solution with hydrochloric acid, and allowing it to stand 24 hours. The tungsten is deposited almost quantitatively in the form of fine white needles of paratungstate.

"Crystals of ammonium paratungstate are insoluble in water, and cannot therefore be further purified by recrystallization. They may however be decomposed by treatment with acid, dissolved in caustic soda or potash solution, decomposed by heat, or reduced to metallic tungsten by hydrogen. The first of these methods is usually adopted as the next step in obtaining pure tungstic oxide. 100 kg of crystals are added in small quantities to 120 liters of 40 per cent hydrochloric acid solution, which is then brought to boiling for 2 hours. The crystals are decomposed according to the equation:

$$5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O + 10HCl \rightarrow 10NH_4Cl + 10H_2O + 12WO_3$$

After settling, the spent acid is syphoned off, and the tungstic oxide is washed repeatedly by decantation. This oxide can now be further purified by dissolving in ammonia and crystallizing again as ammonium paratungstate, or by dissolving in caustic potash and precipitating with hydrochloric acid. For this process 100 kg of tungstic oxide are dissolved in a solution containing 55 kg of KOH in 120 liters of water, and then diluted with water to a specific gravity of 1.12, giving about 900 liters of solution. The precipitation is carried out in wooden vats, or silica vessels. A quantity of hydrochloric acid (sp. gr. 1.2) is first brought to boiling, and an equal volume of the potassium tungstate solution also heated to boiling, is run in at the rate of about 1 liter per minute. Under these conditions a coarse yellow oxide is obtained that is readily washed. The character of the tungstic acid is very much affected by the conditions of precipitation, and particularly by the temperature and concentration of the solutions. It is important that the tungstate should be run into the acid, and not *vice versa*.

"The tungstic acid is finally washed several times with distilled water by decantation, and then collected on vacuum filters which dry it to a hard cake containing 50 per cent WO_3. The cake is transferred to open silica basins and dried at 200° before being ground and sieved.

"The crystallization process may be modified by the addition of potassium or sodium hydroxide to the ammonium tungstate solution, when crystals of the double salts.

$$2Na_2O \cdot 3(NH_4)_2O \cdot 12WO_3 \cdot 15H_2O$$

and

$$2K_2O \cdot 3(NH_4)_2O \cdot 12WO_3 \cdot 15H_2O$$

are obtained. Both the ammonium paratungstate and the double salts are soluble in potassium or sodium hydroxide, and this is made use of in decomposing the crystals. Instead of direct decomposition by boiling with acid, they may be dissolved in caustic soda, the ammonia driven off by heat, and the alkaline tungstate solution run into boiling acid. This method has the advantage of removing the last trace of iron, which is precipitated by the caustic alkali, and permitting better control over conditions of precipitation, thus enabling the desired degree of fineness in the oxide to be obtained. On the other hand, the tungstic acid produced in this way contains 0.1–0.3 per cent NaCl, and the method is not suitable if alkali-free oxide is required.

"Crystals of ammonium paratungstate can be converted into tungstic oxide by heating in air. At 60° the salt loses both water and ammonia, being converted into the meta-tungstate, whilst above 250° decomposition into ammonia, water and tungstic oxide is complete.

"If the crystals are heated in a current of hydrogen at 500-750° the decomposition is accompanied by reduction of the tungstic oxide, and the first stage of reduction, as far as WO_2, is sometimes accomplished in this way."

II. 3. Precipitation as Calcium Tungstate

Sodium tungstate obtained from wolframite is sometimes purified first by precipitation as calcium tungstate. Calcium chloride solution (sp. gr. 1.16) is used for the conversion thus:

$$Na_2WO_4 + CaCl_2 = 2NaCl + CaWO_4$$

The white precipitate formed is thoroughly washed by repeated decantation with water.

II. 4. Treatment with magnesium salts

John B. Ekeley and William B. Stoddard. U. S. Patent 1,322,485 (1919), British Patent 122,264 (1919). By this method, phosphorus and arsenic are removed from the crude sodium tungstate solution. To the solution an oxidizing agent such as sodium hypochlorite is added. Then a magnesium salt, either magnesium sulfate or magnesium chloride, is added in a quantity sufficient to combine with the phosphorus and arsenic acid present. This results in the formation of magnesium hydrogen phosphate, $MgHPO_4$, which is rather insoluble in water. "The solution is thoroughly boiled for about three hours and is allowed to cool to about 60°. This results in the production of normal magnesium phosphate $Mg_3(PO_4)_2$. The solution is thereupon rendered slightly ammoniacal by the addition of 60 pounds of commercial ammonia, and if desired, by the further addition of 10 pounds of ammonium chloride, the amounts added being sufficient, however, to combine the remaining phosphates and arsenates carried in solution, and is then agitated in any suitable manner. As a result ammonium magnesium phosphate, NH_4MgPO_4, is formed as a precipitate. The solution is then allowed to stand for several hours and is filtered from the precipitate. Arsenic compounds similar to the phosphorus compounds mentioned are precipitated and separated at the same time with the phosphorus compounds. The resulting solution contains substantially pure sodium tungstate, substantially free from any traces of phosphorus and arsenic."

II. 5. **As Tungsten Sulfide**

For further purification of the ammonium paratungstate, the solution is treated with hydrogen sulfide[24], when ammonio-sulfo-tungstate is precipitated. This salt is slightly soluble in cold water and is orange red in color. On heating the salt the trisulfide is formed, which may be roasted to tungstic acid. The sulfo-tungstate remaining in solution may be treated with hydrochloric acid in excess which precipitates the pure trisulfide.

C. H. Fischer. British Patent 17,603 (1912). On treating the potassium tungstate solution with double its quantity of ammonium sulfide, the impurities such as iron, zinc, etc., which may be present in the solution, are separated out as sulfides of the various metals, the tungsten remaining in solution as a polysulfide (WS_3). After filtering, the filtrate is treated with hydrochloric acid for the precipitation of the WS_3, which, upon roasting in the air, changes to tungsten trioxide according to the reaction, $WS_3 + 9O \rightarrow WO_3 + 3SO_2$.

II. 6. **Treatment with benzidin hydrochloride**

The alkaline tungstate solution is first neutralized with hydrochloric acid. It is important to add the acid in such quantity as to give approximately a molecular ratio $HCl/WO_3 = 1.5$. The acidified solution is then fractionally precipitated by a solution of benzidin hydrochloride ($HCl \cdot NH_2C_6H_4 \cdot C_6H_4NH_2 \cdot HCl$). The impurities present appear to be largely concentrated in the first fraction. The second fraction, containing the bulk of the WO_3, is pure. The tungsten precipitate is benzidin metatungstate, $C_{12}H_8(NH)_2 \cdot 4WO_3 \cdot xH_2O$. Washing the benzidin metatungstate and calcining it at a low temperature give pure WO_3, which is very fine and fluffy, suitable for the manufacture of pure filaments.

II. 7. **Treatment with Ferro-silicon**

J. L. Furey. U. S. Patent 2,255,210 (1941). Molybdenum is separated from scheelite ore containing it as an impurity, by treating the ore with hydrochloric acid in the presence of ferro-silicon. It has been found that hydrogen slowly liberated by the interaction between ferro-silicon and hydrochloric acid is effective in preventing the precipitation of molybdenum in dilute acid solution. As an example, a scheelite ore containing 53.5 per cent tungsten and 2.26 per cent molybdenum (as MoS_2) was roasted to convert the molybdenum sulfide to oxide. "A charge consisting of 50 parts by weight of the roasted ore, ground to pass a 200 mesh screen (0.074 mm opening), was intimately mixed with 5 parts of ferro-silicon (containing about 15 per cent silicon) ground to pass a 100 mesh screen (0.015 mm opening). This mixture was leached with 130 parts of concentrated hydrochloric acid (about 36 per cent) in a suitable tank for seven hours, the solution so formed being maintained at a temperature of about 40° throughout the leaching operation. The solution was then boiled for about one-half hour, diluted with water to twice its original volume, and filtered to separate the tungstic acid precipitate from the acid solution containing molybdenum. During the filtering step the residue was thoroughly washed with water. An analysis of the residue showed it to contain 57.94 per cent tungsten and only 0.09 per cent molybdenum."

II. 8. As Tungsten Oxytetrachloride

Gin's Method[25]. Tungstic acid obtained by means of the processes described may be purified by having it converted into a volatile tungsten compound. The crude material is dried and blended with a mixture of ferric sulfate and sodium chloride. On heating the mixture for a short time below 400°, the following reactions take place:

$$3Fe_2(SO_4)_3 + 6NaCl \rightarrow 3Na_2SO_4 + 2FeCl_3$$

$$3WO_3 + 4FeCl_3 \rightarrow 3WOCl_4 + 2Fe_2O_3.$$

The oxytetrachloride $WOCl_4$ melts at 210° and boils at 227°. The condensed $WOCl_4$, when thrown into water, is almost immediately decomposed into tungstic acid and hydrochloric acid: $WOCl_4 + 2H_2O \rightarrow WO_3 + 4HCl$. In case the tungstic acid is contaminated with Fe_2O_3, which is formed when any ferric chloride carried over with the volatile $WOCl_4$ comes into contact with the decomposing water, the condensed product may be distilled at 230° leaving behind the FeCl, which boils at 280°.

III. PRODUCTION OF TUNGSTEN POWDER

Tungsten is used commercially in two ways, either in the form of tungsten sheet, wire, etc., or in the form of alloys. In the first case the powder used must be technically free from impurities, and the state of its subdivision is of prime importance. For alloying, some latitude is allowed in the amount of impurity present in the powder, and the state of its subdivision is of minor importance. For the production of the pure metal the hydrogen method of reduction is universally adopted. Other methods for obtaining metallic tungsten, such as reduction with carbon, reduction with metals, electrolytic reduction, etc., may be adopted when simplicity and economy in the process favor its adoption and the requirement as to purity of the product is not strict.

III. 1. Reduction of tungstic oxide with hydrogen.

During the process of the reduction of tungstic oxide with hydrogen, the tungstic oxide passes through all states of oxidation before being reduced to the metal. The reaction for the whole reduction is as follows:

$$WO_3 + 3H_2 \rightleftarrows W + 3H_2O$$

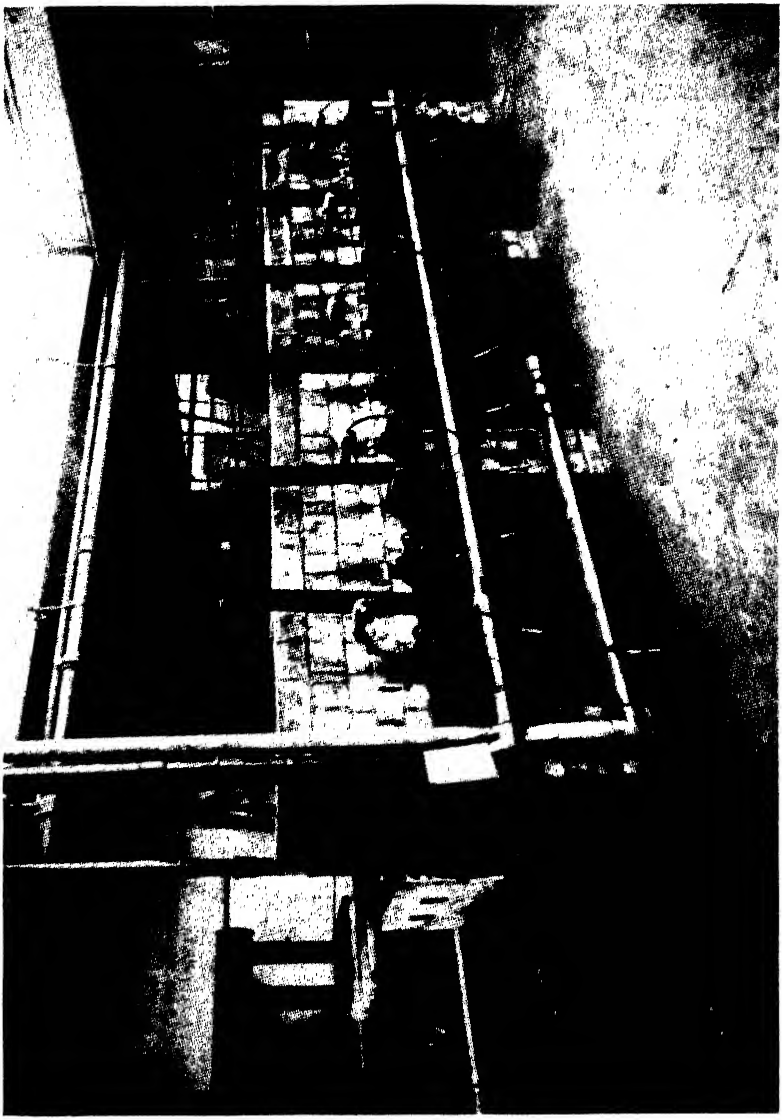
If the vapor formed is continuously removed from the reduction chamber and hydrogen is supplied pari passu, the reaction should proceed toward the right, resulting in tungsten free from the oxide.

In general practice, the initial temperature is usually about 550° and the final temperature 780–1100°, according to the particle size required.

The procedure is to carry out the reduction in two stages. In the first stage the object is to produce the brown oxide, WO_2 at slightly lower temperature. This is then mixed with an equal weight of yellow oxide, WO_3, and the complete reduction is attained at a slightly higher temperature.

"Reduction[26] is usually carried out by a continuous process, in which iron or nickel boats charged with the oxide, are fed through a tube furnace. These furnaces may be heated either by gas or electricity. A typical design of gas-fired furnace is shown on p. 188. The furnace, which is built of fire brick, is about 12 feet long, and has from six to twelve 2-inch iron tubes built into it. Heat is supplied by the fifteen burners seen on the near side in the photograph, which are connected to gas and compressed air mains. Five thermocouples are inserted through the furnace wall with their hot junctions in contact with the furnace tubes, enabling the temperature to be accurately controlled. A temperature gradient is maintained from one end of the furnace to the other, which, during the first stage of reduction, when brown oxide is produced, is from 500 to 700. The tungstic oxide is spread in a thin layer on the bottom of the boats, which are introduced at the cooler end and gradually pushed through the iron tubes, against the hydrogen steam which enters from the other end of the tubes in the opposite direction (on right, of figure). Owing to the large volume of hydrogen used in this process, it is usual to lead it through purifiers after it leaves the reduction tube, and circulate it again. The projecting portions of the tubes at the high-temperature end are water-cooled, so that each boat may be removed, after traversing the length of the furnace, without interrupting the process. The second stage of reduction consists in reducing the mixed oxides to metal, the temperature of the furnace being raised to give a gradient from 650 to 800°.

"A battery of electric furnaces is shown on p. 189. The principle of operation is the same. In the first stage of reduction the temperature gradient in the furnace is from 520 to 720, and boats carrying about 50 grams of yellow oxide are fed in every 12 minutes. In the second stage the furnace temperature is raised to 650–800°, and the boats are charged with 50 grams

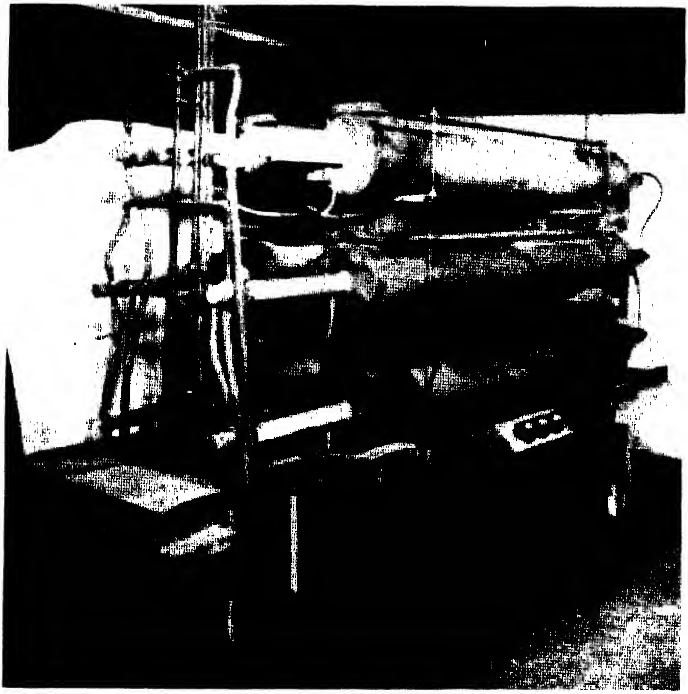


Gas-fired furnace for reduction of tungstic oxide. *From C. P. Smithells' "Tungsten".*

of the mixed oxides. A flow of hydrogen of about 600 liters per hour is maintained in the direction opposite to that in which the boats travel.

"The product of reduction is a grey powder, slightly caked into lumps. These are broken up and passed through a fine silk sieve, any coarse material being rejected."

Tremendous differences in density and particle size can be produced by changes in temperature, rate of hydrogen flow and stoking time. In any such critical operation some inequalities may occur, so that it is a standard practice to assemble fairly large batches of metal powder, and then thoroughly tumble and mix them in order to have practical size lots of uniform properties. The powder is generally screened as soon as removed from the furnace and stored in air-tight containers to prevent oxidation of the finely divided powder and to keep out moisture, which may not only cause oxidation but which causes the material to cake and interferes with screening and pressing. For this reason some manufacturers handle and store the finished powder in air-conditioned rooms.



Battery of electric furnaces for the reduction of tungstic oxide. *From C. P. Smithells' "Tungsten".*

Badische Anilin and Soda-Fabrik in Ludwigshafen; German Patent 261,819 (1911); **C. Bosch and A. Mittasch.** U. S. Patent 1,175,693 (1916). Tungstic acid can be quickly reduced by hydrogen at 500 to 600° under a pressure of 80 atmospheres. If the tungstic acid is mixed with a reducible oxide of other metal, an alloy of the two metals is obtained.

The General Electric Co. British Patent 214,662 (1925). A preliminary fusion of the oxide does seem to make it more suitable for the production of the powder. A solution of tungstic acid in ammonia is treated with hydrochloric acid at boiling temperature, and the tungstic acid thus obtained dried at a temperature at from 120–150°. The dried product thus obtained is formed into bars under high pressure, which are then heated to a dark red heat in porcelain tubes in a current of air. The fusion of these bars is subsequently made by means of a blow-pipe (oxy-hydrogen gas). The fusion treatment tends to harden the oxide into tablet-shaped crystals. By reducing the ground crystals with hydrogen at the comparatively low temperature of from 80 to 900°, tungsten in a fine crystal form, suitable for use in the manufacture of tungsten wire, is obtained.

(a) **Reduction of tungstate and complex tungstic acid.** Sodium tungstate, Na_2WO_4, is reduced by hydrogen at 900°[27]. According to Liempt[28], the complete reduction takes place at 1100° thus:

$$Na_2WO_4 + 3H_2 \rightarrow W + 2NaOH + 2H_2O.$$

A. de Graaf. German Patent 379,317 (1922). Silico-tungstic acid, boro-tungstic acid or their salts are reduced by hydrogen.

J. Schilling. German Patent 249,314 (1908). Ammonium tungstate is reduced to very fine powder by hydrogen at a temperature slightly higher than its decomposition temperature.

(b) **Addition of substances to influence recrystallization of the metal during reduction by hydrogen.** It has been found that the intentional addition of certain substances, such as the alkaline oxides, silica, boron and the oxides of thorium, uranium, calcium, etc., has a marked influence on the recrystallization of the tungsten metal produced. This subject will be taken up under the section on filament.

(c) **Ernst Pokorny.** U. S. Patent 1,877,961 (1932). Ores of the wolframite group are subjected to the action of a mixture of hydrogen and chlorine in the ratio of 8 to 1 respectively, at between 850 and 950°. The results obtained are that the iron and manganese content of the ore are volatilized in the form of their respective chlorides, whereas the tungsten contained in the ore is reduced and left behind in the metallic form.

III. 2. Reduction of tungstic oxide or of tungsten ore with carbon

Reduction of tungstic acid with carbon is now confined to the production of crude tungsten powder for alloys. Since the metal produced by this method is always contaminated with a certain amount of carbide and other mineral substances contained in the carbon used, it is not suitable for use where extreme purity is demanded. According to Davis[29], the reduction of tungstic acid by carbon undergoes several successive steps before the final metallic product is obtained: at 650 to 850° the tungstic oxide changes to a blue or purple oxide, a mixture of WO_2 and W_4O_{11}; at 900 to 1050°, the brown oxide, WO_2, is formed; and at temperature above 1050° the gray tungsten powder results.

The reduction is generally carried out in graphite or fireclay crucibles[30]. It is important to prevent ingress of air into the charge, by having the covers luted on with clay or by protecting the charge with a mixture of pitch and lampblack. The tungstic oxide used must be thoroughly dried; otherwise the steam given off during reduction would disrupt the charge. Lampblack is the best form of carbon used for the reduction, as it is low in ash and free from alkalies, sulfur and iron. In order to lower the carbon content of the metal, the amount of carbon used should not exceed 12 to 14 per cent of the weight of the WO_3, although the theoretical amount required is 15.5 per cent. The addition to the mixture of colophonium, amounting to 10 to 30 per cent of the carbon required, favors the intimacy of the tungstic oxide and lampblack while being mixed by shaking or ball-milling. The charge is heated to 1300–1400° during 8 hours, held at this temperature for another 8 hours, and then slowly cooled. The product generally contains 92–98 per cent tungsten, which may be purified by crushing and washing with water on tables.

It may be of interest to state that G. Charles Wheeler in 1915 commercially reduced WO_3 with granulated sugar.

(a) **Reduction of tungstic oxide: C. M. Johnson.** U. S. Patent 964,868 (1910); German Patent 246,182 (1910). The WO_3, and carbon, instead of being mixed together, are charged in separate successive layers, whereby the gas phase of the carbon in the form of CO developed reduces the WO_3, thus producing a carbon-free metal.

(b) **Reduction of tungstates: C. J. Head.** British Patent, 155,600 (1920). Ground sodium tungstate is thoroughly mixed with ammonium chloride and carbon, both being in excess. The mixture is heated in a suitable vessel to between 1000 and 1100° and is so maintained for 12 to 15 hours. The following reaction takes place:

$$2NH_4Cl + Na_2WO_4 + 3C \rightarrow 2NH_3 + 2NaCl + H_2O + 3CO + W$$

The output of efficiency is between 70 to 80 per cent of the tungsten content of the charge, the balance being distributed between the lower oxides remaining unreduced and soluble tungstates, which may be reclaimed by washing and precipitation.

W. Mafert. U. S. Patent 946,551 (1910). Sodium paratungstate ($Na_2W_2O_7$) is mixed with carbon in the proportion of 500 to 35 parts by weight. The mixture is heated to redness in a slowly revolving furnace until CO_2 starts to evolve. At this point, H_2 or water gas is admitted until complete reduction is reached. The product is washed with slightly alkaline water, then with dilute HCl, and finally with water.

(c) **Reduction of Tungsten Ore.** The direct reduction of tungsten ores with carbon yields a product which is only suitable for alloying with steel, while the percentage recovery of tungsten is low. The following are the patents covering this method of reduction:

C. M. Johnson (U. S. 977,096 [1910])
C. M. Johnson (German 246,182 [1910])
J. C. Butterfield (British 16,562 [1915])
J. C. Butterfield (U. S. 1,217,913 [1917])
D. J. Giles (U. S. 1,348,356 [1920])

III. 3. Reduction of tungstic oxide or tungsten ore with metals or their compounds.

A number of processes have been developed for the reduction of tungstic oxide or of tungsten ore with metals or chemical compounds, but it does not appear that any of them is likely to be of any technical importance.

(a) **Aluminum:** Powdered aluminum easily reduces tungstic oxides according to the following reactions:

$$WO_3 + Al_2 \rightarrow W + Al_2O_3$$

$$3WO_2 + Al_4 \rightarrow 3W + 2Al_2O_3$$

This alumino-thermic method is also known as the Goldschmidt process. To prevent the formation of the alloy WAl_4, a slight excess of WO_3 is required. The slight excess of WO_3 forms with the Al_2O_3 the tungstate of aluminum [probably $Al_2(WO_4)_3$], which is insoluble in water.

According to L. Weiss and A. Martin[31], aluminum reacts with calcium tungstate (scheelite), producing metallic tungsten, thus:

$$CaWO_4 + 2Al \rightarrow W + CaO \cdot Al_2O_3$$

O. Voigtländer. U. S. Patent 1,224,242 (1917). A mixture of WO_3 and Al, placed in a suitable receptacle, is heated in a furnace to as high a temperature as possible, so that by the heat of reaction of the mixture combined with that supplied by the furnace, the resulting tungsten metal conforms to the shape of the containing vessel.

Aktien Gesellschaft B. Felder-Clement. British Patent 187,375 (1922). Ten kilograms of tungstic oxide are charged and rammed tightly in a crucible; above the oxide is placed 2.5 kilograms of aluminum in the form of a cast plate. The crucible so prepared is heated to about 1700°. When reaction is completed, metallic tungsten is formed at the bottom of the crucible, weighing about 7.5 kilograms; above it lies a dense layer of the corundum (aluminum oxide) formed.

(b) **Zinc:** Experiments on the reduction of tungstic acid with zinc were carried out by L. Kahlenberg and H. H. Kahlenberg[32]. The method of procedure was to add H_2WO_4 to a fusion of equal parts of NaCl and KCl, and then treat the fused mass with zinc dust. The amount of H_2WO_4 taken was one-half of the weight of the NaCl-KCl mixture. The proportions of zinc and H_2WO_4 used were according to the following equation:

$$H_2WO_4 + 3Zn \rightarrow H_2O + 3ZnO + W$$

After half an hour of heating at a temperature of 800°, the fusion mixture was cooled and extracted with NaOH and then with dilute HCl. The yield of metallic tungsten was 67 per cent of the theoretical in the experiment.

The so-called Delphine Process[33] involves reduction of tungstic acid or ammonium tungstate with zinc. A mixture of tungstic acid and pulverized zinc, agglomerated with tar and pressed into the form of small pellets, was charged into a retort heated by producer gas. The reduction took place easily at a temperature between 900 and 1,000°.

Zirkon-Glühlampenwerk Dr. Hollefreud & Co. (German Patent 221,899 (1910); **H. Zerning** (U. S. Patent 1,019,581 (1912)). In these two patents, tungstic oxide is first reduced with zinc and then the reduction product is further treated with magnesium or aluminum.

(c) **Calcium: H. Kuzel and E. Wedekind.** French Patent 419,043 (1909); U. S. Patent 1,088,909 (1914). The reduction of tungstic oxide with calcium is carried out in a vacuum.

M. N. Rich. U. S. Patent 1.738,669 (1929). The reduction of tungstic oxide is carried out in an hermetically sealed container with a mixture of calcium chloride. calcium and a proportion of calcium-magnesium alloy.

A. S. Cachemaille. British Patent 238,663 (1925); **J. W. Marden.** U. S. Patent 1,704,257 (1929). The reducing agents employed are an alkaline-earth metal, preferably calcium, and a halide of the same alkaline-earth metal. The reduction is carried out in a bomb from which oxygen and nitrogen are excluded.

(d) **Magnesium: J. W. Marden.** U. S. Patent 1,602,542 (1926). The reduction of tungstic oxide with magnesium is carried out in a bomb which is heated to a temperature above 600° to start the reaction. The reaction then progresses without the aid of external heat, as the heat of reaction is sufficient to reduce the oxide.

(e) **Sodium:** E. Zettnow[34] heated a mixture of tungstic oxide and sodium under a layer of fused sodium chloride in an iron crucible. To remove the alkali salts and iron, the reduction product was treated with water and dilute hydrochloric acid.

F. G. Keyes. U. S. Patent 1,270,842 (1918). Dry liquid ammonia is first used to dissolve the sodium required. When the sodium is completely in solution, tungstic oxide is added and the mixture is stirred. The ammonia is then distilled from the mixture of sodium and tungstic acid. When the mixture is ammonia-free, it is slowly heated to about 500 to 600° and maintained at that temperature until the reaction is completed.

(f) **Silicon, Silicide, Carbide:** Silico-Thermic Process[35]. The mixture of tungsten silicide, tungstic acid and calcium oxide is charged into an induction furnace. The reaction of the mixture is as follows:

$$W_2Si_3 + 2WO_3 + 3CaO \rightarrow 4W + 3CaSiO_3$$

The energy density should not be less than 1,200 to 1,500 watts per cubic decimeter of metal contained in the channels of the furnace.

Electric Furnaces and Smelters, Ltd. German Patent 247,993 (1912). A mixture consisting of 75 parts of tungstic oxide, 7 to 10 parts of ferrosilicon and 14 to 18 parts of calcium carbide is fused in an electric furnace when tungsten metal is produced.

F. M. Becket. U. S. Patent 930,027 (1909). Silicon and boron are used to reduce the tungstic oxide in an electric furnace.

(g) **Titanium: J. B. Huffard.** U. S. Patent 992,422 (1911). The method of reducing tungstic acid with titanium or its compounds is based upon the following reactions:

$$2WO_3 + 3Ti \rightarrow 2W + 3TiO_2$$
$$2WO_3 + 3TiN \rightarrow 2W + 3TiO_2 + 3N$$
$$WO_3 + 3TiO \rightarrow W + 3TiO_2$$
$$WO_3 + TiC \rightarrow W + TiO_2 + CO$$

III. 4. Treatment of Tungsten Sulfide

The reduction of tungsten sulfide with hydrogen at a temperature of 795–1065° yields a metal free from oxygen, sulfur and carbon, according to the formula:

$$WS_2 + 2H_2 \rightleftarrows W + 2H_2S$$

According to L. Weiss and A. Martin[36], treatment of WS_3 with CaO in an electric-arc furnace results in a metal containing 88.29 per cent W; using a graphite crucible, the resulting product contains 98.96 per cent W.

E. A. Lederer. U. S. Patent 1,659,205 (1928). The reduction of tungsten sulfide with carbon is carried out in a vacuum electric furnace. The heating is started around 800° and gradually increased to about 1500°, which is maintained for about one-half hour.

III. 5. Treatment of Tungsten Chloride

Tungsten chloride, whose production has been treated under I. 10, can be reduced to the metal with hydrogen or with carbon at between 1000 and 1500°.

C. C. Buré. French Patent 522,718 (1920). Chloride or oxychloride of tungsten is reduced to the metal by treatment with water gas at 1200°.

H. C. P. Weber. U. S. Patent 1,373,038. By treating the volatile chloride of tungsten with iron within the range of temperatures between 700–1200°, tungsten metal is formed. while the chlorine radical of the chloride combines, by substitution, with iron to form ferric chloride. The iron and chlorine used in the process may be regenerated by treating the ferric chloride with carbon.

J. W. Marden. U. S. Patent 1,437,984 (1922). Instead of employing iron. as is done in Weber's patent, aluminum is used for the reduction of the chloride.

J. W. Marden. U. S. Patent 1,573,083 (1926); 1,646,734 (1927). A mixture of sodium and calcium chloride or of any alkaline-earth halide and an alkali metal is used as the reaction agent for the treatment of the chloride and oxychloride of tungsten in a bomb. The mechanism of the reaction is that, although sodium alone reacts on the chloride, a combination of sodium and calcium chloride is necessary to reduce the oxychloride.

III. 6. Electrolysis

The problem of obtaining metallic tungsten by electrolytic reduction has been attacked by numerous investigators, who invariably tried to use either tungstic oxide or alkaline tungstate as the primary material. Although the processes they have developed may possess some potential usefulness in certain particular problems in the future yet at present none of them appears likely to lend itself to economic development.

Dr. C. C. Ma[37a,b], has succeeded on a laboratory scale, in the direct production of tungsten metal from ore by means of electrolizing a bath of fused alkali borate or alkali phosphate with tungsten ores.

"For the fused borax bath using wolframite as the source of tungsten, the results were: (1) best composition of electrolyte, 1.5 parts $Na_2B_4O_7$ per 1.0 part of ore concentrate; (2) operating temperature. 1,050° to 1,300°; (3) optimum current density, 50 amp/dm^2; (4) best current efficiency obtained, 78.23 per cent; (5) best yield, 417.5 g/kw-hr; and (6) best quality of tungsten produced, 99.57 per cent W.

For the fused phosphate bath using wolframite as the source of tungsten, the results were (1) best composition of electrolyte, 1.75 parts phosphate mixture (7 moles $Na_4P_2O_7$ + 3 moles $NaPO_3$) per 1.0 part of ore concentrate; (2) operating temperature, 1,050 to 1,300°; (3) optimum current density, 50 amp/dm^2; (4) best current efficiency obtained, 80.96 per cent; best yield, 505.1 g/kw-hr; and (6) best quality of tungsten produced, 99.7 per cent W."

(a) **Electrolysis of Aqueous Solutions of Tungstates.** The electrolysis of aqueous solutions of tungstates does not usually lead to the production of tungsten powder *per se*, but results only in plating a thin layer of tungsten on metallic cathodes. The subject has been extensively investigated, but so far no practical process has been developed.

Jackson, Russell and Merrill[37] have obtained tungsten powder at a mercury cathode by using a 4.6 *N* hydrofluoric acid solution, a current density of 65 to 100 amp/dm^2, and maintaining the bath at 95°. Using 2 cc. of mercury as cathode, only a few milligrams of tungsten were obtained in a run of 8 hours.

Halt and Kahlenburg[38] obtained the following optimum results from numerous experiments on plating brass or copper cathodes with tungsten:

Electrolyte: 35 to 500 grams of sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) per liter, in which 60 to 120 grams of WO_3 were dissolved.

Temperature: 90°.

Current density: 10 amp/dm^2.

Maximum thickness of deposit: 0.02 gram/dm$_2$ for 15 minutes or 2 hours.

Current efficiency: less than 1 per cent.

Neuman and Richter[39] have obtained small deposits of tungsten by electrolyzing solutions of tungsten hexachloride in glycerin. The efficiency is low.

Nickel-tungsten deposits, containing 5 to 10 per cent of tungsten, have been obtained by M. L. Holt and M. L. Nielsen[39a], by using the Watts type of nickel plating bath which was modified by the addition of small amounts of sodium tungstate. The composition of the bath used was: $NiSO_4 \cdot 7H_2O$, 250 g/1: $NiCl_2 \cdot 6H_2O$, 21 g/1; and H_3BO_3, 30 g/l. Sodium tungstate was added to the nickel plating bath from a stock solution containing 71.7 g/l of $Na_2WO_4 \cdot 2H_2O$. In order to prevent precipitation of any basic nickel tungstate that may be formed, the pH of nickel plating bath was controlled by H_2SO_4 to below 5.4 before the sodium tungstate solution was added. Metallic deposits were obtained at 0.2 amp/dm^2, and those obtained at 50° and particularly those at 70° were more metallic in appearance than the lower-temperature deposits.

Iron-tungsten alloys have been obtained by M. L. Holt and Rodney E. Black[39b] from an ferrous ammonium sulfate iron plating bath which was modified by the addition of small amounts of sodium tungstate. It was found that the tungsten content of the alloy increased somewhat with: (a) increase in tungsten content of the bath; (b) decrease of cathode current density; (c) increase of bath temperature; and (d) decrease of bath pH. The most satisfactory alloy deposit was obtained from a bath containing 1 to 2 gl of added tungsten. The best conditions of electrolysis are: (a) a rather high current density; (b) a bath pH of 2; and (c) a bath temperature of 75°. The authors advanced the theory that the reduction of tungstate ion at the cathode is due to the action of atomic hydrogen and/or by "unstable, active" iron.

Wolfram Lampen Akt-Ges. German Patent 237,014 (1911). By electrolyzing a solution of WCl_6 in acetone, tungsten metal is deposited on the cathode of platinum, nickel or carbon.

Wolfram Lampen Akt-Ges. German Patent 231,657 (1911). A solution of pertungstic acid ($WO_3 \cdot H_2O_2 \cdot H_2O$) or its salt in water, alcohol or ether is electrolyzed: temperature: 20 to 25°; volts, 10 to 20; cathode: platinum, nickel, copper, or carbon.

J. J. Berthet. French Patent 539,234 (1921). Through electrolyzing a solution of potassium or sodium tungstate, with mercury in contact with the cathode, an alloy of tungsten and mercury is obtained. By heating this alloy at 800°, tungsten metal is obtained while the mercury is recovered.

R. E. Pearson, E. Neville and Durelco, Ltd. British Patent 181,837 (1922). Powdered tungstic oxide is mixed into a paste with dilute sulfuric acid. The paste is introduced into the cathode porous pot, immersed in the electrolyte of sulfuric acid. With a voltage of 6 to 7 volts, nascent hydrogen is produced which effects the reduction of the oxide. The powder produced is in a state of very first subdivision.

C. G. Fink and F. L. Jones. U. S. Patent 1,885,701 (1932); 1,885,702 (1932). Sodium tungstate, prepared in about the proportions of 330 grams of sodium carbonate to 125 grams of tungstic acid per liter of solution is electrolyzed at 100° with a platinum anode and a brass cathode and a current density of 200 amp per sq ft of submerged cathode area. Instead of sodium tungstate, a solution of lithium tungstate or ammonium paratungstate can be used. The tungsten plating can proceed only up to a certain degree of thickness and then almost stops. However, if the solution contains nickel carbonate ($NiCO_3$), the plating process continues without stopping. Naturally the nickel is co-deposited with the tungsten. But by circulating the electrolyte, the percentage of nickel in the plated area can be so controlled that it amounts to little more than 0.001 per cent by weight.

H. H. Armstrong and A. B. Menefee. U. S. Patent 2,145,745 (1939). Marignac[40] states that when normal or metatungstates are dissolved in hydrofluoric acid. compounds of the metal fluorides with tungsten dioxydifluorides are formed. These salts are usually soluble in water. It is found that when a bath contains compounds of the metal fluorides with tungsten dioxydifluorides (WO_2F_2), deposits of alloys of tungsten can be obtained by electrolyzing such bath with tungsten carbide or tungsten alloy carbide anodes. It is contended that the radical WO_2F_2, which would ionize as $(WO_2)^{++}(Fe_2)^{--}$, is responsible for the plating.

The process of electroplating with tungsten alloys involves the following points: using tungsten carbide or tungsten carbide alloys; dissolving tungsten dioxide (WO_2) in an aqueous acid fluoride bath; adding an acid-soluble salt of a metal of group 8, series 4 of the Periodic Table to be alloyed with the tungsten to the bath; adjusting the pH of the bath to between 4.5 to 6.8; maintaining the bath at a temperature between 35° to 80°, with a current density of about 14 amp per sq ft of submerged cathode area.

(b) **Electrolysis of Fused Bath.** In the electrolysis of fused alkali bath, the maintenance of the alkalinity or the acidity or the neutrality of the melt determines the type of product obtained. A neutral or slightly alkaline melt gives rise to the production of tungsten powder: an acidity exceeding 5 per cent WO_3, at 585–670°, the so-called tungsten bronzes, which will be discussed in the next chapter; an acid melt at 1020° gives a coherent deposit for electroplating.

Production of Tungsten Powder

Liempt[41] has investigated the electrolysis of a fused bath of the tungstates. By the electrolysis of Li_2WO_4, Na_2WO_4 and K_2WO_4 or a mixture of these at between 900 and 1000°, using a neutral or slightly alkaline melt, tungsten powder is obtained. A current efficiency of 60–80 per cent is obtainable. According to Burgers and Liempt[42], by the electrolysis of a melt containing 19 mole-per cent K_2WO_4, 35 mole-per cent Na_2WO_4 and 46 mole-per cent Li_2WO_4 at a temperature of 500°, using a current density of 6 amp per sq cm, tungsten is obtained in the α and β modifications. By heating this product at 900° in a stream of hydrogen gas the powder completely changes to the β modification.

Kahlenberg[43] obtained pure tungsten by the electrolysis of a fusion mixture of equal parts of NaCl, KCl, and H_2WO_4 between carbon electrodes, using a current density of 0.5 amp per sq cm and a potential drop of 3 volts. L. Andrieux[44] obtained tungsten metal by electrolysis of a melt of WO_3 in B_2O_3. NaF, $Na_2B_4O_7$, heated at 1000 to 1200°, using high current density. According to L. Weiss and A. Martin[45], a fusion mixture of WO_3

with cryolite is readily electrolyzed with a current of 250 amp and 13 to 14 volts. The resulting powder contains 96 per cent of tungsten. In the electrolysis of fused barium tungstate with a current of 250 amp at 20 volts. the resulting powder after treatment with dilute nitric acid, water and aqueous ammonia, contains 89.58 per cent tungsten.

By using a bath, consisting of tungstic oxide dissolved in a mixture of pyro- and metaphosphates of sodium and sodium chloride, Hartmann[46] has developed a process [German Patent 514,365 (1930)] of seemingly commercial importance. S. T. Leo and T. N. Shen[47] have made further investigation of this process and have determined the following optimum conditions of composition of the bath, temperature and current density:

Bath: $Na_4P_2O_7$.......... 7 moles
$NaPO_3$........... 3 "
WO_3............. 4 "
NaCl.............15 "

Temperature: 900°.

Current density: 35 amp per dm^2.

Although the addition of NaCl decreases the current efficiency, its addition tends to increase the conductivity of the bath, thus reducing the power consumption used. Under the above conditions, 469.9 grains per kilowatt-hour are obtained; after washing, the product contains 99.87 per cent W.

F. G. Keyes and R. B. Brownlee. U. S. Patent 1,202,534 (1916); 1,202,535 (1916). This method of obtaining tungsten metal consists in heating the tungsten trioxide to a temperature of about 2000°, thereby producing a lower oxide or a mixture of oxides which conducts electricity readily even at ordinary temperatures. By electrolyzing a fusion of this lower oxide, tungsten metal is obtained.

N. V. Philips' Gloeilampen-Fabricken. British Patent 236,152 (1925). An alkali-metal tungstate is electrolyzed above 900°, to which both an alkali oxide or hydroxide (preferably the peroxide) is added to prevent the formation of tungsten bronze, which is caused by an excess of WO_3 in the bath.

F. G. Keyes. U. S. Patent 1,293,117 (1919). The electrolyzing bath consists of dissolving tungsten trioxide in boric acid at 1200 to 1400°.

F. H. Driggs and J. W. Marden. U. S. Patent 1,821,176 (1931). The fused bath is composed of an alkali-earth metal chloride, such as calcium chloride, containing a proportion of a double halide of tungsten, such as tungsten potassium chloride, and a proportion of tungsten oxide.

Electroplating from Fused Tungstate Bath. In order that the process of electrolysis of fused salt may be applied to electroplating, it is important to maintain the bath in an acidic condition; and to prevent the formation of tungsten bronze, the melt must be maintained at a sufficiently high temperature.

By electrolyzing a fusion mixture, containing 38 per cent Na_2WO_4, 32 per cent Li_2WO_4 and 30 per cent WO_3, the following results were obtained by van Liempt[48]:

At 585–670°, tungsten bronze was deposited.

At 835–870°, a little tungsten was deposited.

At 1020°, a good deposit of tungsten was obtained.

To quote from Smithells[49]: "The best results are obtained with a melt consisting of $Li_2WO_4 \cdot nWO_3$ where n may be from 0.2 to 0.8. The melt must be kept at 1000° or higher to avoid the production of lower bronzes, and the current density should be from 20 to 80 amp per dm^2. Using a fusion of 90 per cent Li_2WO_4, 10 per cent WO_3 at 1340°, a deposit 30 μ in thickness is obtained in about thirty minutes. This is capable of taking a high polish, and is so adherent that the metal may be bent without cracking the plating. It has excellent heat- and acid-resisting properties.

"The thickness of the deposit which may be obtained in one operation is limited to 30–100 μ. When the cathode is withdrawn from the fusion, it is covered with bronze, which can be removed with a steel brush, revealing the plating underneath. A further deposit may now be made on this surface, and the process repeated to any desired thickness. This peculiarity throws some light on the nature of the reaction taking place, and has been explained by van Liempt in the following way. Tungsten bronze, when heated, decomposes according to the equation:

$$3Na_2W_2O_6 \rightarrow 3Na_2O + 5WO_3 + W$$

and the reaction is reversible. The first product of electrolysis is tungsten bronze, but when this has attained some thickness it is no longer in contact with the acid melt, the reaction goes towards the right, and tungsten is deposited. This may explain why the best results are obtained with lithium, since lithium bronzes are the least stable, and most easily decomposed".

N. V. Philips' Gloeilampen-Fabricken. British Patent 236,153, (1925). Using lithium tungstate and maintaining its fusion at above 900°, with a current density of 75–100 milliamp per cm^2, at 0.08 volt, an adherent deposit is obtained.

III. 7. By Thermal Decomposition

The formation of the chlorides and oxychlorides of tungsten has already been discussed under II. 10. The hexachloride decomposes when heated above 1600° C into tungsten and chlorine, thus: $WCl_6 \rightarrow W + 3Cl_2$. In the presence of H, the decomposition occurs at above 1000°, thus: $WCl_6 + 3H_2 \rightarrow W + 6HCl$.

J. Schilling. U. S. 950,869 (1910). When meta- or paratungstate of ammonium is heated at a sufficiently high temperature, in an non-oxidizing atmosphere of ammonia gas or nitrogen, the ammonium radical of the compound is wholly or partly dissociated into hydrogen and nitrogen. The nascent hydrogen thus produced, reduces the oxide of tungsten to metallic tungsten.

RECAPITULATION

Decomposition of Tungsten Ore

The use of sodium carbonate for fusion in a rotatory furnace has been generally adopted for wolframite ore. However, digestion with caustic soda under pressure would form an ideal process for the treatment of such ore. For scheelite ore, decomposition with acids, preferably hydrochloric acid. is the usual practice. Acid treatment of wolframite and alkali treatment of scheelite do not generally give satisfactory results.

However, for scheelite alone, its decomposition may be effected by fusion with a combination of sodium carbonate and carbon according to the following reaction:

$$2CaWO_4 + 2Na_2CO_3 + 2C \rightarrow 2NaWO_3 + 2CaO + 4CO$$

Methods of decomposition with ammonia, bisulfate, sodium sulfate, fluoride, carbon tetrachloride, alkali sulfides, etc., have not so far lent themselves to practical application.

The methods based on calcium carbonate and sodium chloride depend on the chemical interchange of these so-called neutral salts into calcium chloride and sodium carbonate, which thus puts this procedure right back to the original chemical reaction based on soda ash.

Many modifications in the production technique have been made, the principal ones being:

(1) Changes in the ratio of ore to soda ash.
(2) Replacement of all or part of the soda ash with caustic soda.
(3) Changes in furnace design.
(4) Changes in fusion temperatures.
(5) Additions of other chemicals to fusion mixtures.
(6) Use of autoclaves.

Purification of Tungstic Acid

Methods of precipitation are numerous, but the use of hydrochloric acid is predominant in any commercial process. Sometimes small amounts of nitric acid and/or sulfuric acid are added to the hydrochloric acid used. It is not possible to lay down a hard and fast rule for precipitation procedure. Concentration of solutions, temperature, rate, etc., are more or less dependent upon the particular grade of the tungstic acid desired, since all these factors influence the physical properties of the final product.

The purification methods as described under II. 2 are both practical and efficient. For extreme purity, several purifications may be required: but, if the original crude tungstic acid is carefully washed with distilled water, treated with ammonia under carefully controlled conditions using laboratory cleanliness, and finally evaporated and crystallized, in either enamel or stainless-steel vessels, the primary product can be made to a purity of 99.92 per cent.

Production of Tungsten Powder

As the production of pure tungsten products lies in the specialized field of powder metallurgy, in which the material is never molten, but is merely pressed and sintered into an ingot, the physical, as well as the chemical properties of the original powder are of the utmost importance. The control of these properties originates in the intermediate tungsten compounds preceding the actual production of the powder. Practically all pure tungsten compounds, as contrasted to the alloys such as steel, are produced by the reduction in hydrogen of tungsten oxides, either directly from the trioxide WO_3 or from the oxides resulting from the decomposition of ammonium paratungstate by heat, either alone or in the presence of hydrogen. The control of these basic materials is therefore essential to the production of the desired characteristics in the metal powder.

Each of the steps, described under II. 1 and II. 2, properly controlled, constitutes a purification process and the flow sheet finally adopted will depend on the original impurities in the raw material and the degree of final purity required. The final product, whether precipitated oxide, or one or the other of the paratungstates will depend on the physical characteristics which are being sought. Generally speaking, precipitated oxides will be softer, less dense and contain a larger range of particle sizes; the paratungstates will be denser and more uniform in size, with the paratungstates produced by evaporation generally considerably coarser than the needle form produced by neutralization. Each producer has his own preferences; many using more than one type of oxide, either separately or blended, to give him the metal powders which he prefers for his variety of final metal product. It should be mentioned here, that there is no universally accepted criterion, for metal powder characteristics. Since tungsten is always "cold worked", in the technical sense, the size of the original ingot, the amount of reduction to the final size, and the selection of annealing points all enter the problem and influence to a greater or less degree the selection of the original powder.

For the production of the pure metal the hydrogen method of reduction is universally adopted. Reduction of tungstic acid or oxide with carbon was formerly the standard procedure for all tungsten alloys used in the steel industry. At that time, a crude powder containing probably an average of 90 per cent W was produced by various methods, but largely by reduction with charcoal, lampblack, or petroleum coke in crucibles. In the period from about 1915 to 1920, ferro-tungsten completely replaced this crude powder as an additive agent and for some years little or no tungsten powder was produced by carbon reduction.

While tungsten powder other than that prepared by hydrogen reduction has never been satisfactorily used in the production of wire, rod, and sheet, many uses for tungsten powder of slightly lower purity and somewhat different physical properties have opened quite a field for carbon- or gas-reduced powder. Consumption of this grade of powder, principally for hard facing metals, welding rod, etc., has, during the past few years, amounted to several hundred tons annually. It has been possible to produce commercially tungsten powder containing as low as 0.10 per cent carbon and as high as 99.70 per cent W by other hydrogen-reduction methods. Production of tungsten powder by reduction with Al, Ca, Mg, Zn or Na, etc., has not yet arrived at a stage where it can be commercially adopted.

Electrolysis, as a process for the production of metallic tungsten, using either fused bath or aqueous acid and alkaline solutions, has not yet developed to a point where it can lend itself to economic development. However, continued research along these lines, especially with fused bath in the direct treatment of the ore, may develop some worthwhile application.

MANUFACTURE OF DUCTILE TUNGSTEN

In connection with the manufacture of ductile tungsten, attention should be drawn to Section III. 1 (p. 186) which treats of the reduction of tungstic oxide with hydrogen.

The successful manufacture of ductile tungsten depends in a great measure upon the purity as well as the particle size of the oxide and the powder employed. The purity of both the oxide and the powder is primarily conditioned by the quality of the ore used for their manufacture. Any impurities which once get into the oxide will eventually contaminate the resulting powder. Hence only the purest kind of tungsten ore is used for the manufacture of tungsten rods and wires. Sykes[50] states: "The particle size of the tungsten powder is one of the most vital factors which enter into the control of the product. This in turn is dependent upon the state of the oxide and the reduction conditions, such as the temperature and the purity of the hydrogen. The control of this factor is even now based upon rules which are mainly empirical in origin.

"It has been fairly well established that, for one important class of material at least, the following relations hold:

"1. A fine oxide produces a fine metal powder and conversely a coarse oxide results in a coarse metal powder, under like conditions of reduction.

"2. A metal powder of small particle size tends to produce a treated bar of relatively large grain size, while the coarser metal powder results in a smaller grain size. Grain size and orientation is a matter of prime importance to the filament, as is well known.

"A tungsten powder which is too coarse or 'sandy' will not consolidate well under pressure, while a very 'fluffy' metal will be too soft to handle after pressing. It is sometimes necessary to add a little paraffin dissolved in carbon tetrachloride to the metal to improve its pressing characteristics. Generally speaking, the best working properties are obtained in a metal which has a maximum number of particles of size about 0.010 mm with a fairly rapid decrease in frequency down to 0.003 mm as finest and up to 0.017 mm as coarsest."

According to Smithells[51], the particle size of the tungstic oxide intended for the manufacture of ductile tungsten varies from 0.5 to 5.0 μ. "In the decomposition of tungstate solutions by acid the following effects are noted:

"1. Temperature: the colder the solutions, the finer the oxide.

"2. Concentration: more concentrated solutions of either acid or tungstate give coarser oxides.

"3. Rate of mixing: The more slowly the ammonium tungstate solution is added, the finer the oxide.

"The particle size of an oxide can also be controlled after precipitation by varying the temperature of drying, and subsequent firing. Calcining the dried oxide at 650° causes a definite increase in the size of the particles, and this becomes more pronounced at higher temperatures."

Generally speaking, a fine metal powder of a grey-black color with an average particle size of about 1 to 3 μ is employed for the manufacture of ductile tungsten.

Particle size of the powder depends upon the following factors:

1. Temperature
2. Time of reduction
3. State of the original oxide
4. Amount of water vapor in the hydrogen used.

The following table[52] shows the conditions for producing different particle sizes:

Diameter of particles (μ)	Type of furnace	Maximum temperature °C	°F	Hydrogen	Weight of WO_3 per cc in tube (grams)
0.5	Continuous	800	1470	Dry	0.05
2.0	Continuous	830	1525	Dry	0.5
4.0	Continuous	900	1650	Dry	1.0
8.0	Intermittent	1130	2065	Saturated with water at 75°C (165° F)	1.5
10.0	Intermittent	1200	2190	Saturated with water at 85° C (185° F)	2.0

Process. The processes as used by different manufacturers today for the manufacture of ductile tungsten are based on the invention of W. D. Coolidge. His patents [British 23,499 (1909); U. S. 1,082,933 (1913)] for making ductile tungsten from the metal powder by suitable heat treatment and mechanical working have formed the basis of later developments and have practically superseded such old-time processes as the organic binder and coating processes of Just and Haunaman, or the colloidal method of Kuzel and the amalgam process.

The manufacture of ductile tungsten (filament wire) consists of the following successive operations:

1. Pressing
2. Sintering
3. Treating
4. Swaging
5. Wire Drawing
6. Wire Annealing and Cleaning

1. **Pressing.** The metal powder is first thoroughly mixed by tumbling and sifted through a 250-mesh screen. A weighed amount is then loaded into a steel mold and subjected to a pressure of 20 tons per sq in. In wire manufacture the pressed bar is usually 24 in long by $\frac{1}{2}$ or $\frac{3}{4}$ in square. The size of compact intended for the fabrication of x-ray electrode or electrical contact depends upon the size of the finished product. To strengthen the bar for handling, some binding material is sometimes incorporated, such as water, glycerin or a solution of paraffin wax in benzene.

Because of the difficulty of removing the weak compact from the mold, the mold is designed so that the sides may be removed and the compact freed without lifting or bending.

2. **Sintering.** The pressed bar is too fragile to be handled with ease. Therefore, it is carefully transferred to a slab of tungsten, molybdenum or carbon and stoked into an electric furnace consisting of an Alundum muffle wound with a molybdenum heating element. The bar is heated to 1000–1200° for about one-half hour in a hydrogen atmosphere. At the back of the muffle is a water-cooled chamber in which the bar is cooled to room

temperature. The bar thus sintered, although still very brittle, is now strong enough to be handled, and has an apparent density of about 12 or 13.

3. **Treating.** Although the bar now appears solid, it still lacks any definite crystalline form. Therefore the next step is to produce the desired crystalline structure and remove the voids which still exist between the particles of powder. This operation is known as "treating". For this treatment the sintered bar is suspended vertically from a water-cooled clamp while its lower end is clipped to a copper or molybdenum contact which is immersed in a water-cooled well of mercury. This arrangement is enclosed in a water-cooled copper hood, which dips into a ring of mercury, and dry hydrogen is passed through the enclosure.

This method of suspending the bar and connecting it in the electric circuit results in the partial cooling of the ends of the bars, with the result that both ends of the bars are under-treated and somewhat porous, and therefore are unworkable and must be broken off and discarded. Hence a number of different methods have been developed for so-called "butt-treating", which eliminates this loss.

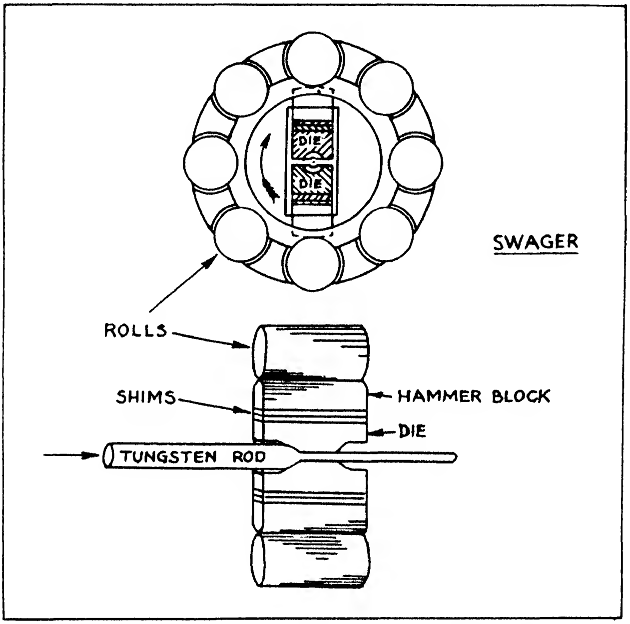
Current is then passed through the bar and is maintained at 85–95 per cent of the amperage required to fuse the bar, as determined by a previous test. The treating schedule, *i.e.*, the rate at which the current is raised to the final treating point, and the time the current is maintained, is determined by the nature of the original powder, the amount and nature of the impurities present and the crystal structure desired.

During this operation the bar shrinks considerably from 12 to 18 per cent, depending on the treating schedule, the type of metal, the load applied when pressing, etc., and the density rises to between 16.5 and 18.5. This operation further purifies the metal, as the high temperatures obtained volatilize most materials, and the resulting bar is very definitely crystalline and metallic.

The control of this operation is determined by the structure of the bar as determined under the microscope, a definite grain count, *i.e.*, number of grains per square millimeter, being established for the ingot, depending on what type of material is to be produced.

4. **Swaging.** After the above operation, the bar is strong but very brittle at ordinary temperatures. However, at elevated temperatures it becomes malleable, and can be rolled or hammered. For the production of rod and, wire the next step, therefore, is to hammer these bars in swaging machines in which they are gradually reduced in diameter. A diagrammatic drawing of a swager is shown herewith.

The two halves of the die, which are rapidly rotated about the axis of the tungsten rod, fly apart by centrifugal force and are returned by the impacts from the surrounding ring of rollers. Thus the rod receives about ten thousand blows per minute. Most swagers are equipped with feed rolls which move the bar steadily through the machine so that it is uniformly worked. As it is customary to reduce the rod about 12 per cent at each pass, it is obvious that many operations and many dies are required to reduce it to about 1.0 mm, at which size it may be drawn.



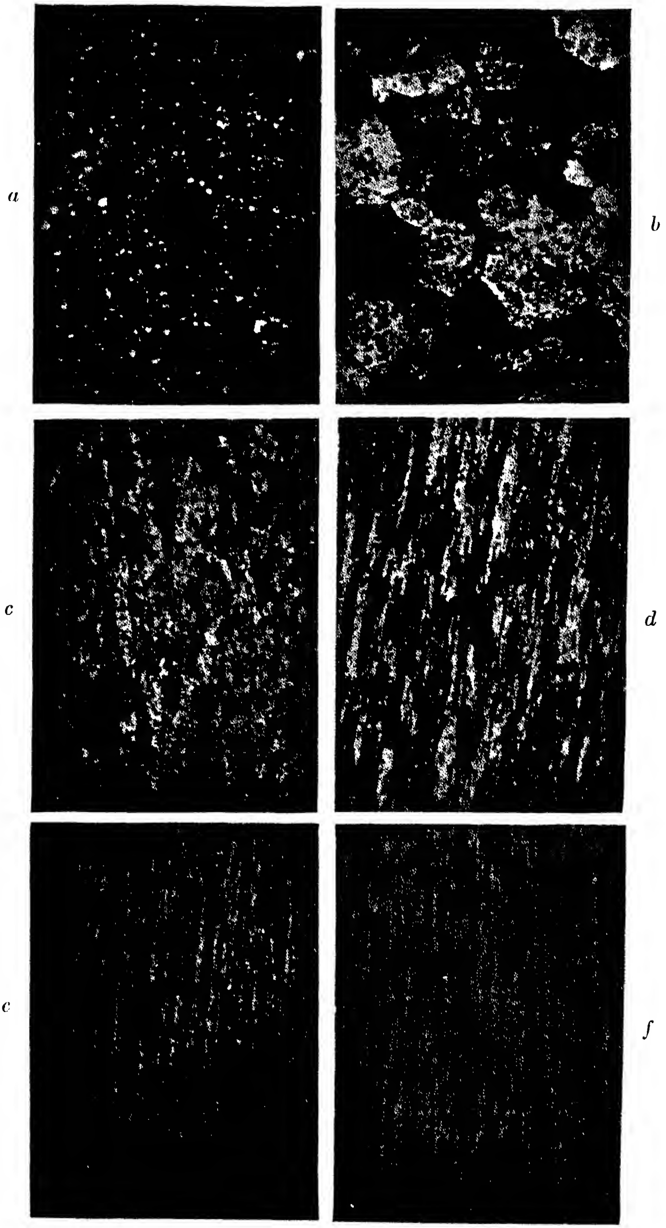
Diagrammatic drawing of a swager. *After Sykes.*

The initial swaging operations are begun around 1500 to 1600° and are then gradually reduced as the diameter decreases, as follows[53]:

Wire Diameter (mm)	Swaging Temperature (°C)
11 to 6	1350
5.5 to 2.5	1250
2.5 to 1.0	1175
1.0 to 0.05	800–550

As tungsten is readily oxidized at these temperatures it is generally protected by a coating of graphite, which is applied in the early stages and periodically renewed.

Continued working in this manner gives rise to the development of a fibrous structure in the tungsten, and it is this fibrous structure which imparts ductility and toughness to the wire. When the original bar is quite



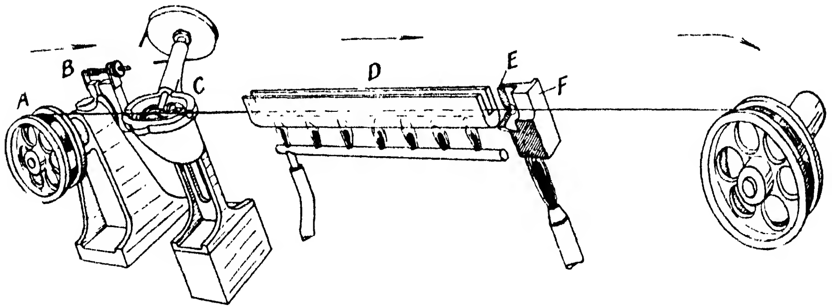
Etched sections showing changes in structure of a tungsten bar during working. *a* = Pre-sintered bar. *b* = Sintered bar. *c* = Swaged rod, 5 mm diameter. *d* = Swaged rod, 2 mm diameter. *e* = Swaged rod, 1 mm diameter. *f* = Drawn wire, 0.5 mm diameter. *After C. P. Smithells.*

large with respect to the finished product it is sometimes necessary to "re-treat" the rod to restore some of the original crystalline structure, in order to continue with the swaging operation.

5. **Wire Drawing.** Tungsten is generally swaged until the rod reaches a diameter of 0.10″ or less, after which further reduction is by means of drawing through a die, as shown.

The drawing operation is carried out under heat, even into the finest sizes, temperatures being gradually reduced as the diameter decreases. In addition to heating the wire, the die itself is also heated.

The drawing dies are generally made of tungsten carbide or of diamonds, the former being used for wires down to about 0.010 and diamond dies for the smaller sizes. As in the swaging operations, the wire is protected by a coating of colloidal graphite, which not only prevents oxidation but also acts as a lubricant for the wire passing through the die.



Arrangement of tungsten-wire drawing machine. *A*, take-off drum; *B*, brake; *C*, aquadag pot; *D*, heater; *E*, die; *F*, heated die-block. *From C. P. Smithells' "Tungsten".*

6. **Wire Annealing and Cleaning.** Wire is sometimes annealed during the drawing process in order to control its properties for special applications. Final annealing is also frequently required for wire which must be specially formed or otherwise fabricated. This operation, generally achieved by heating in hydrogen, also removes the graphite coating, giving a clean wire. If wire is to be cleaned without annealing, particularly the larger sizes of rod, this may be done by dipping in fused Nitrite; fine sizes may be cleaned electrolytically by making the wire one electrode of a D.C. circuit in a bath of caustic soda.

Control of Recrystallization in Drawn Wire. The control of the crystalline structure of the drawn wire is important if the wire is destined to be used as filament in incandescent lamps. In the days of the straight filament lamp, the phenomenon of "offsetting" formed one of the chief causes of failure of such filament. "Offsetting" was due to the growth of large grains in the glowing filament during use, resulting in the development of grain boundaries extending across the full diameter in a plane at right angles to the long axis of the wire. It can be prevented by introducing into the metal small proportions of either alumina and silica (usually 0.1 per cent Al_2O_3 and 0.1 per cent SiO_2), as is done in the Battersea Process, or thorium nitrate (usually about 0.75 per cent). These "additives" serve the purpose of mechanical obstruction to grain growth.

Nowadays coiled filament takes the place of straight filament in gas-filled incandescent electric lamps. In order to maintain the efficiency of the filament, the coil must keep its shape, that is, it must not "sag" at the high temperature of about 2500°. To prevent "sagging", the structure in the filament should be one of extremely large and long grains. It was Dr. Aladar Pacz who first discovered that large-grained, sag-resisting structure was obtained by introducing fractional percentages of alkali silicates into the tungstic oxide before reduction.

Materials such as silica, silicates, silico-tungstates, boron, soda, potash, lime and barium, often in conjunction with thoria, are added to tungstic acid before reduction. Usually the additives used are composed of silico-tungstate of sodium or potassium, mixed with a non-volatile substance such as SiO_2, Al_2O_3 or ThO_2. No satisfactory explanation of the action of these additives has been given, but it is possible that these substances, in a volatile form, may possess the influence of "cleaning up" the surfaces of the tungsten grains, thus permitting to a greater extent the play of the inter-surface forces. However, according to P. E. Wretblad[54], the following explanation is suggested: "The alkali components permit exaggerated grain growth at temperatures near their decomposition points. At such temperatures, which may indeed be quite low, diffusion across grain boundaries becomes more probable and exaggerated grain growth is possible in various directions. However, with the other component of the double additive, this effect is only possible at very high temperatures (for ThO_2, 2500°); thus, when used alone, this type of additive tends to inhibit grain growth during processing of the wire at fabricating temperatures. It follows, then, that when additives of the proper amount are used in conjunction, exaggerated grain growth may occur in a preferred direction, because, during drawing of the wire, the inhibiting material has been extended as stringers parallel to the wire axis, and lateral diffusion or change in atomic orientation in a lateral direction is less probable. Thus, at elevated temperature, diffusion and grain growth persist in the longitudinal direction and grain-boundary surfaces tend to favor an acute-angle orientation with the axis of the wire. As mentioned before, this geometrical relationship of grain-boundary surface to the axis of the films tends to prevent offsetting during subsequent use of the filament."

The following is a list of some of the patents covering the use of additives in the control of crystalline structure in coiled filament.

The British Thomson-Houston Ltd., British Patent 155,851 (1921); use of silica and alkalies.

The General Electric Co., Ltd., British Patent 186,497 (1922); use of thoria and alkalies.

Siemens Brothers and Co., British Patent 188,706 (1922); use of thoria and boron.

The British Thomson Houston Co., Ltd., British Patent 202,001 (1923); use of two alkalies, one of which is potassium, rubidium or cesium.

Aladar Pacz, U. S. Patents 1,280,825 (1918); 1,299,017 (1919); 1,410,499 (1920); 1,468,073 (1922); use of silica and magnesium.

Naamlooze Vennootschap Philips' Gloeilampenfabricken, British Patent 216,124 (1924); use of alkali salt of a chromium, oxygen, or manganese oxygen compound.

C. J. Smithells, U. S. Patent 1,559,799 (1925); use of thoria and alkalies.

A. S. Cachemaille, British Patent 239,742 (1925); use of alkalies and lithium oxide.

C. G. Fink, U. S. Patent 1,675,486 (1928); use of zirconium and copper.

F. H. Driggs, E. S. Patent 1,965,222 (1934); use of potassium chloride and silicate.

A. E. MacFarland, U. S. Patent 2,078,182 (1937); use of potassium fluotitanate ($K_2TiF_6 \cdot H_2O$) and alkalies.

C. A. Laise, U. S. Patent 2,202,108 (1940); use of rhenium and vanadium.

TUNGSTEN CARBIDES[55–62]

Tungsten carbide, W_2C, as a compound, was prepared by Moissan as early as 1896, by reducing tungstic oxide with carbon in an electric furnace. It was not until about 1919 that Lohman made tool and die materials, chiefly of tungsten carbide. In 1927 Krupps patented a mixture of cemented tungsten carbide with up to 10 per cent cobalt under the name Widia, which is the basis of the modern tools for machining ferrous and non-ferrous metals and non-metallic materials, such as bakelite, porcelain; glass, etc.

Carbides of Tungsten

The existence of tungsten carbide, WC, and di-tungsten carbide, W_2C, is definite, but there is some doubt about that of other carbides represented by W_3C, W_3C_2 and W_3C_4.

The fundamental reactions between tungsten and carbon may be thus represented:

$$2W + C \rightleftharpoons W_2C$$

$$W + C \rightleftharpoons WC$$

For the preparation of W_2C, it is necessary to heat the mixture at 1000 to 1600° in an atmosphere free from carbon; WC is prepared at 1500–1600° in an atmosphere free from air but slightly carburized. Tungsten carbide may also be prepared by reducing tungstic oxide directly with carbon or by carbonizing tungsten metal powder with carbon monoxide, methane or other hydrocarbons.

The important physical properties of the carbides are as follows:

	W_2C	WC
Density	17.15	15.52–15.67
Melting Point	3130±50° K	3140±50° K
Hardness (Mohs scale)	9–10	+9

According to W. P. Sykes[60], tungsten carbide, WC, containing 6.12 per cent carbon, forms a eutectic with W_2C at a temperature of 2525°, and finally itself decomposes at 2600°, yielding a tungsten-rich liquid and solid carbon. Obviously these temperatures determine the upper limit of temperature in the manipulation of this material.

The studies made by Wyman and Kelley with regard to the reactions of tungsten carbide with cobalt in connection with the use of cobalt as a binder show that the lowest successful sintering temperature of a mixture of tungsten carbide and cobalt is about 1350° and that these materials form a liquid eutectic phase at that temperature. Apparently the molten eutectic alloy thus formed becomes the true cementing material in tungsten carbide products, wetting the larger tungsten carbide grains which are left over after the smaller grains are absorbed by the cobalt. Accompanying the formation of this eutectic alloy is the growth of the large tungsten carbide grains, which assume sizes many times greater than the largest particles originally present in the material. The cobalt content of the cemented carbide alloys varies in practice from 12 to 3 per cent and the sintering temperature employed accordingly rises from 1350 to above 1400°.

Hoyt[60] summarizes some of the properties of cemented tungsten carbide as follows:

Properties of Cemented Tungsten Carbide

Cobalt (%) →	3	6	9	13	20	100
Density, grams per cc at 21°	15.04	14.82	14.56	14.10	12.54	8.62
Rockwell A hardness, on C scale with 60-kg load		90		87		
Vickers Brinell number	1380	1450	1365	1255	755	280
Shore monotron number	190	145		130		
Modulus of rupture, (lb per sq in)						
Electric resistance, microhms per cc at 20°	21.3	21.1	22.3	19.6	29.2	9.84
Temperature coefficient of resistance, for interval 20 to 30°	0.0047	0.0045	0.0043	0.0041	0.0038	0.0036
Coefficient of expansion, (average per °C over interval 20 to 400°)				6.0		

Strength.[60] The following figures show that for a carbide containing 13 per cent cobalt, its strength is well maintained even at red heat.

Temperature (°C)	Modulus of Rupture (kg/mm²)
20	174
800	137
850	127
900	105

Modulus of Elasticity.[60] The following figures demonstrate that cemented tungsten carbides possess a higher elasticity than any other known material.

	Modulus of Elasticity (kg/mm²)
Cemented Tungsten Carbide (13% Co)	60,000
Tungsten	34,000
Steel	20,000

	Torsional Modulus of Elasticity (kg/mm²)
Cemented Tungsten Carbide (13% Co)	13,000
High-speed steel	6,250

Manufacture of Cemented Tungsten Carbides

1. **Cold-Pressing Method.** (a) *Preparation of tungsten carbide.* The tungsten powder used must possess the appropriate particle size, as the properties of the ultimate product are greatly influenced by its size, which varies generally from 3 to 8 μ. After ball-milling with the necessary amount of lampblack to form WC, the mixture is heated in a carbon tube for 2 to 3 hours at about 1500°. Other methods of carburization consist

in heating the mixture in gas-fired furnaces lined with silicon carbide and Corundum, and in producing the carbide from direct reduction of tungstic acid with carbon.

The carbide thus produced is crushed, milled and sieved. The maximum particle size of the sieved product is about 20 μ; the maximum number of particles occurs at about 2 μ.

(b) *Preparation of cobalt powder.* Cobalt powder is manufactured by reduction of the oxide in hydrogen at below 800°. The control of the temperature is necessary to obtain the requisite particle size.

(c) *Ball-milling.* The incorporation of cobalt with the carbide is affected by ball-milling in a steel bottle, which is about 8½ in diameter and 10 in long, rotating at approximately 60 rpm. The balls employed are made either of sintered tungsten carbide or of steel. The time of milling is never less than 10 hours and may be as much as 60.

The proportion of cobalt required depends on the intended application of the final product. Generally, the cobalt required amounts to 5-10 per cent of the tungsten carbide used. With increasing cobalt the strength of the final product increases while the hardness decreases.

(d) *Pressing.* Pressing of the ball-milled powder in molds can be greatly facilitated by the addition of up to 1 per cent of glycerin or paraffin wax dissolved in a suitable solvent (*e.g.*, carbon tetrachloride). A pressure not higher than 30 tons per square inch is employed.

(e) *Prefiring.* The molded articles are subjected to a prefiring treatment at between 800 and 1000° for approximately 30 minutes. This treatment leads to a sintering of the cobalt and tends to strengthen the articles so that they can be handled and shaped with ease by means of Carborundum wheels, or by the usual operations of turning, drilling or filing.

(f) *Sintering.* The shaped articles, packed in alumina, are finally sintered at 1400–1500° for 30–60 minutes in a hydrogen atmosphere. Another method is to sinter the articles in carbon tubes. The time and temperature employed depends on the cobalt content of the article in question. During the operation a shrinkage of 12 to 20 per cent in linear dimension occurs.

2. **Hot-Pressing Method.** The advantages of the hot-pressing method are that the porosity of the product is substantially reduced and that the complete sintering at high temperature takes only a very short time. The preparation of the mixed carbide and cobalt powders follows the procedure as outlined above. The carbide-cobalt mixture is introduced into a carbon mold which may be heated by direct passage of current through it, and pressure is applied simultaneously. The heating time is

not more than one second and the pressure is usually more than 1000 lbs up to 2,500 lbs per sq in. Only articles of a simple shape are manufactured by this method.

For the manufacture of non-symmetrical cross shapes, such as angles, half-rounds or screws, the extrusion process was recently adapted.

Steel machining with cemented tungsten carbide has given rise to difficulties which, in the main, are due to "cratering", and to the welding or "pick up" of particles of the tool metal on the rapidly moving steel chip. To overcome these difficulties, tantalum and/or titanium carbide is incorporated as an additional binding agent in the manufacture of cobalt cemented tungsten carbide.

Much work has gone into research to improve the strength and hardness of the commercial carbides with the result that compositions of practically carbides with the result that compositions of practically identical chemical analysis but widely differing properties have been developed. A major feature of these investigations has been the demonstration of the effect of particle size on the properties of the finished metal. This is plainly indicated in the article by Comstock on German Carbides on page 224. Grades *G1* and *H1* are practically identical in analysis but *H1* which is definitely harder is considered a different carbide and is recommended for a different class of work.

Meyer and Eilender demonstrated that several modifications in processing also derive from the particle size. Namely a lower pressure is needed for forming the compacts; a lower sintering temperature and an increase in hardness all result from the use of finer particle sizes.

Methods of grinding the carbide, wet versus dry mixing of carbide and cobalt, and the use of lubricants and protective films are all features of the art and the accuracy and skill with which these various factors are controlled are vital to the production of a uniform material of predictable performance properties.

With the development of a demand for large quantities of identical pieces such as tool tips, tablet making machines have come into use supplanting the older hydraulic press, and with it has come additional problems such as producing materials with good flow characteristics for filling the molds, and uniform shrinkage of the compacts during heat treatment.

Kennametal, an intermetallic compound of the formula $WTiC_2$ (U. S. Patent 2,113,353-6) is a recent tungsten carbide. Its manufacture has been described by P. M. McKenna[61], its inventor, as follows: "This compound is synthesized in a metallic menstruum, or bath of nickel, at a temperature above 2000° by heating tungsten and titanium with graphite in a graphite crucible. Only in this way was the compound formed, for

Hardness, Strength and Conductivity of Kennametal

Property	Alloy Designation KH	 KM	 KS
Hardness, Rockwell A (a)	91	90.3	89.9
Rockwell C (b)	78	76.5	75.7
Transverse rupture strength (c)	224,000	275,000	310,000
Thermal conductivity (d)	0.075	0.110	0.120

(a) A scale, 60-kg load.
(b) Diamond penetrator, 150-kg load.
(c) Rectangular bar, 0.200 in thick by 0.375 in wide, supported on line centers 9/16 in apart. Strength computed by beam formula from load at failure.
(d) Calories per sec per °C per cm.

Physical Properties of Some Commercial Cemented Carbide Compositions*

Composition	Density g/cc	Rockwell Hardness A Scale	Transverse Rupture psi	Young's Modulus psi $\times 10^6$ (b)	Compressive Strength psi (c)	Proportional Limit in Compression psi (d)	Impact Strength ft-lb (e)	Endurance Limit psi (f)	Coefficient of Thermal Expansion (g)
97% WC, 3% Co	15.25	92.7	170,000	97.5	815,000	780,000	—	—	—
95.5% WC, 4.5% Co	15.05	92.3	200,000	90.5	890,000	740,000	—	—	—
94% WC, 6% Co	14.85	90 to 92	225,000	88	750,000	600,000	0.73	95,000	5.0×10^{-6}
91% WC, 9% Co	14.60	89.5 to 91.5	275,000	—	685,000	540,000	—	—	—
87% WC, 13% Co	14.15	87.5 to 90	300,000	80	625,000	525,000	1.10	105,000	5.9×10^{-6}
80% WC, 20% Co	13.55	85 to 87	350,000	—	559,000	425,000	1.75	—	—
Predominantly WC with TaC and 13% Co	13.90	87 to 88	275,000	—	610,000	475,000	—	—	7.25×10^{-6}
Predominantly WC with TaC and 6% Co	14.70	91 to 92	220,000	—	752,000	670,000	0.65	85,000	—
Predominantly WC with TiC and 6% Co	11.20	92 to 93	160,000	—	700,000	—	0.40	90,000	6.8×10^{-6}
Predominantly WC with less TiC than above 8% Co	12.80	91.5 to 92.5	250,000	—	570,000	560,000	0.60	90,000	—
Predominantly WC with larger amount of TiC, 7% Co	9.00	92 to 93	150,000	—	725,000	—	—	—	7.0×10^{-6}
Predominantly WC, with TaC and TiC, 8% Co	11.7	91.5 to 92.5	165,000	72	720,000	—	—	—	6.75×10^{-6}
Predominantly WC, with TaC and TiC, 11% Co	11.6	90.5 to 91.5	175.000	—	680.000	—	0.60	85,000	6.0×10^{-6}
Predominantly WC, with TaC and TiC, 15% Co	11.4	89.5 to 90.5	190,000	67	670,000	—	0.92	—	7.5×10^{-6}

NOTES: (a) the values given in this table are representative of properties obtained in good production practice. They are not necessarily the highest obtainable, nor do they represent the lowest which are of practical use.

(b) Most values for Young's modulus were obtained by W. H. Davenport of the Norton Company by the musical pitch method.

(c) Most of the values for compressive strengths are given through the courtesy of P. W. Bridgman of Harvard University.

(d) Proportional limit in compression is the load per unit area at which the increase in strain ceases to be directly proportional to the increase in stress.

(e) Impact values are from unnotched specimens approximately ¼ in square section; Charpy machine was used.

(f) Values for endurance limits are based on 20,000,000 cycles, for specimens of R. R. Moore rotating beam type.

(g) Average coefficient of expansion per °C for the range 20 to 700° (68 to 1290°F).

* From Wulff's "Powder Metallurgy," p. 446.

the molten nickel provided a solvent in which the three component atoms, tungsten, titanium and carbon, could group themselves into this compound.

“In making Kennametal, the crystals of $WTiC_2$ are pulverized in ball mills with matrix-forming metals such as cobalt and tungsten until the particles are smaller than may be resolved by the best microscope using ordinary light. By hydraulically pressing portions of this mixture in suitable molds, tool tips, balls, cylinders, tubes and other forms are made. The pressed blanks must be larger than the desired finished size to allow for shrinkage, usually about 22 per cent linearly. This shrinkage takes place during the subsequent heat treatment in vacuum furnaces, necessary to obtain the product of very fine-grained, dense tool metal. It is produced in three grades of hardness by altering the percentage of cobalt, the lowest amount of which is 11 per cent Co in the hardest grade ‘KH’. The attached tabulation gives the properties of the three grades.

“The modulus of elasticity in all these compositions is about 58,000,000 lbs per sq in, approximately double that of steel.

“Unlike tungsten carbide cemented with cobalt, which is made by heating the pressed blanks in hydrogen, Kennametal is made in vacuum furnaces, under very definite conditions of temperature and pressure below 40 microns, mercury gage. The finished blanks have a surface appearing like a galvanized steel sheet, that is, with a very thin layer of cobalt condensed like frost on a window pane. This is because the cobalt was vaporizing in the hot furnace chamber at this degree of vacuum.”

It is claimed that the “tool life [of Kennametal] between grinds and re-settings is three to ten times as many pieces as with high-speed steel tools and that the surface speed is two to six times that of high-speed steel tools.”[62]

The following list of patents pertaining to the manufacture of tungsten carbide is taken from Gmelin's “Handbuch der anorganischen Chemie.”

I. Smelting Process

1. *Complete Smelting*

Initial Material	Carbon (%)	Additional Material	Patent
WO_3 and C			Voigtländer & Lohmann Metallfabrikations-Ges. M.B.H. (German 286,184 [1914]) Lohmann-Metall G.M.B.H. (German 335,405 [1918]); British 157,769 [1921]; Swiss 96,340 [1921])
W and B or Si		Mo, Fe, Ti, Ni, Cr	Lohmann-Metall G.M.B.H. (British 157,774

Initial Material	Carbon (%)	Additional Material	Patent
			[1921]; Swiss 96,341 [1921])
WO_3 or W		Th, U, Mo, Ta	H. Lohmann (British 246,487 [1926])
W		5 to 10% ThO_2, 3 to 5% Mo	H. Lohmann (British 348,336 [1926])
Tungsten Carbide and C		Mo, MoO_3	B. Felder-Clement Akt.-Ges. (German 417,392 [1920]; British 185,313 [1921])
40 to 45 part W	2 to 4 parts	30 to 40 parts Fe, 4 to 6 parts Ti, 2 parts Ce. W can be displaced by Mo, Fe by Mn, Co and Ti by Zr, B, Si, U	G. Fuchs, A. Kopietz (German 307,764 [1917])
To 60% W	2 to 4	Fe, Ti, Ce	G. Fuchs, A. Kopietz (German 310,041 [1918])
W	More than 3	Ni	H. K. Sandell (U. S. 1,268,495 [1918])
40 to 50 parts W	2 to 4 parts	4 to 5 parts Ti, 30 to 40 parts Fe, 1 to 2 parts Ce, small quantity of Cr or Ferrochrom	Gesellschaft Fur Wolframindustrie M.B.H. (German 320,996 [1918]; 307,764 [1917]; Swiss 89,279 [1920])
75 to 84 parts W	3 to 5 parts	10 to 15 parts Ti, 2 to 5 parts rare earth Ce, Th, Zr	Gesellschaft für Wolfram-Industrie M.B.H. (German 401,600 [1922])
WO_3 and C		NiS, $CaSO_4$ or CaF_2	Guardian Metals Co. (U.S. 1,698,212 [1922]; 1,702,765 [1922])
W + C (diamond powder)		Ti, Fe	S. Goldstein (British 175,638 [1922])
95.5 to 97% W	3 to 4.5	W can be replaced by Mo, Cr, C by B, Ti, Si	Patent - Treuhand - Gesellschaft für elektrische Gluhlampen M.B.H.; K. Schroter (German 498,349 [1923], General Electric Co.; K. Schroter (U.S. 1,774,849 [1923]; British 213,214 [1923])
W or WC		Mo, U, Ti, Zr, B, Si and Fe, Co, Ni, V as contact body	Gewerkschaft Wallram (German 516,656 [1924]; British 239,499 [1925]; French 603,924 [1925]; Swiss 126,603 [1925])
Tungsten Carbide	3 to 7	Fe, Co, Ni	Patent - Treuhand - Gesellschaft für elektrische Gluhlampen M.B.H.; K. Schroter (Russ. 14,471 [1926])
W and C, B, Si			A. Brennecke (French 622,301 [1926])
Tungsten Carbide		Metal of Pt-group, Co NbC or Nb	W. Schrobsdorff (British 276,011 [1927])

Initial Material	Carbon (%)	Additional Material	Patent
15 to 20 parts W and 3 to 20 parts WO_3			O. L. Mills (U. S. 1,721,966 [1929])
W	2 to 5	Mo, Zr, Co, Ni	Vereinigte Stahlwerke, A.-G. (British 355,782 [1930])
At least 55% W or W and Mo	Up to 2	20 to 40% Cr, Fe, Co, Ni, Mn. Up to 3% B, Si, Al. With not more than 70% W or Mo, 20% Cr must at least be present; in the absence of Cr, more than 70% W or W and Mo must be present.	W. Muller, Prinzessin O. Zur Lippe (British 348,641 [1930])

2. *Partial Smelting*

Tungsten Carbide		Fe	Patent - Treuhand - Gesellschaft fur elektrische Gluhlampen M.B.H. (German 443,911 [1922])
1 to 20% Tungsten Carbide		99 to 80% (1 part Cr and 1 to 2 parts Co)	Siemens & Halske Akt.-Ges., Erfinder B Fetkenheuer (German 427,074 [1922])
Tungsten Carbide		Volatile Metal	General Electric Co.; H. Baumhauer (U. S. 1,512,191 [1927])
Tungsten Carbide		Co, Ni	Cl, A. Laise (U. S. 1,633,258 [1925])
W or Tungsten Carbide		Cr, Co	R. Walter (U. S. 1,803,882 [1927])
Tungsten Carbide		Cr-Co-Alloy, if necessary up to 0.5% B, Ti	R. Walter (German) 521,785 [1928])
Tungsten Carbide and B		Co, Ni	Eisler Electric Corp., A. Laise (U. S. 1,842,103 [1930])
Tungsten Carbide		3.5 to 13% Co	Firth Sterling Steel Co. (French 689,027 [1930])
Tungsten Carbide		Co	Compagnie Française pour L'Exploitation des Procédés Thomson Houston (French 706,829 [1930])

II. Sintering Process

1. *Sintering below Atmospheric Pressure*

Tungsten Carbide		Sinter in carbon mold	Voigtländer & Lohmann, Metall-fabrikations-Ges. M.B.H. (German 289,066 [1914])

Initial Material	Carbon (%)	Additional Material	Patent
Tungsten Carbide		Sinter in iron mold	Voigtländer & Lohmann, Metall-fabrikations-Ges. M.B.H. (German 292,583 [1914])
Tungsten Carbide		Mo, MoO_3	Voigtländer & Lohmann, Metall-fabrikations-Ges. M.B.H. (German 395,926 [1914])
Tungsten Carbide		Sinter in carbon mold	Voigtländer & Lohmann, Metall-fabrikations-Ges. M.B.H. (German 295,556 [1914])
W or Tungsten Carbide or WO_3 and C		Mo, Te, B, Fe, Si, Ni, Cr, Pt, Th, Zr, U	A. J. Liebmann, Cl. A. Laise (U. S. 1,343,976 [1917]; 1,343,977 [1917])
Tungsten carbide	3 to 10	More than 10% Fe, Co, Ni	General Electric Co. Ltd., Patent-Treuhand-Gesellschaft fur Elektrische Gluhlampen M.B.H. (British, 213,524 [1923])
Tungsten Carbide	3 to 7	Up to 10% Fe, Co, Ni	Patent-Treuhand-Gesellschaft fur Elektrische Gluhlampen M.B.H.; K. Schroter (German 420,689 [1923]), General Electric Co.; K. Schroter (U. S. 1,549,615 [1923])
Tungsten Carbide	6.2	10 to 20% Fe, Co, Ni	Patent-Treuhand-Gesellschaft fur Elektrische Gluhlampen M.B.H.; K. Schroter (German 434,527 [1925]) General Electric Co. Ltd.; von Patent-Treuhand-Gesellschaft fur Elektrische Gluhlampen M.B.H. (British 251,929 [1925])
Tungsten Carbide	Up to 3	Fe, Co, Ni, Mn, Cr, Ta	Metallabor Akt.-Ges. (Swiss 126,013 [1927])
Tungsten Carbide		Fe, Co, Ni	F. Krupp Akt.-Ges. (British 279,376 [1927])
W + C		Fe, Co, Ni	F. Krupp Akt.-Ges. (British 278,955 [1927])
Tungsten Carbide		Up to 15% Metalloid or low melting metal	F. Krupp Akt.-Ges. (U. S. 1,757,846 [1928])
Tungsten Carbide		3 to 20% Mn, Manganese steel with 0.25 to 1.25% C	Firth Sterling Steel Co., G. J. Comstock (U. S. 1,815,613 [1928])
Tungsten Carbide		Carbide of Mo, Ti, V, U and Fe, Co, Ni	Siemens Schuckert Werke A.-G.; B. Fetkenheuer (German 520,139 [1928])

Initial Material	Carbon (%)	Additional Material	Patent
W + C or Tungsten Carbide		Fe, Co, Ni	British Thomson Houston Co.; S. L. Hoyt (British 288,521 [1928]; 288,427 [1928])
Tungsten Carbide		Electrolyte Fe, Co, Ni, if necessary, Co, Mn	F. W. Rauth (French 655,216 [1928])
Tungsten Carbon-nitride		Nitride of metals and metalloids	R. Walter (French 656,678 [1928]; British 316,702 [1929])
Tungsten Carbide		Electrolytic coated with Co, Fe, Ni, Cu	Firth Sterling Steel Co., R. B. Welch (U. S. 1,833,099 [1929])
W + C		Ti	F. Krupp Akt.-Ges. (Swiss 141,611 [1929])
W + Carbon		Low Temperature melting metal	F. Krupp Akt.-Ges. (British 310,885 [1929]); Swiss 140,173 [1929])
More than 50% Tungsten Carbide or Tungsten Carbide + Tungsten Carbon-nitride		5 to 30% W, Mo, Cr, and Fe, Co, Ni	R. Walter (French, 685,640 [1929])
Tungsten Carbide	3 to 7	Be	Vanadium Alloys Steel Co.; Ph. M. McKenna (U. S. 1,737,255 [1929])
$WO_3 + C$		CoO	British Thompson Houston Co., (British 346,632 [1930])
WC		Up to 25% Co, Up to 3% ThO_2	British Thomson Houston Co., L. Wyman (British 359,427 (1930])
50 part Tungsten Carbide		7.5 parts U	British Thomson Houston Co.; S. L. Hoyt (British 354,028 [1930])
W_2C		15 to 30% Ta	Vanadium Alloys Steel Co., P. McKenna (U. S. 1,892,653 [1930])
W		SiC, ZrC, TiC, Ce, ThC_2; Fe, Co, Ni	Bayrische Metallwerke A.G. (French 716,659 [1931]; British 387,684 [1931])
WC		2 to 30% of mixed crystals of carbide of elements Group 4 and 5. Up to 20% Fe, Co, Ni	Wolfram und Molybdan A.G. (French 749,190 [1933])
WC-Mo_2C		Fe, Co, Ni	P. Schwarzkopf, Metallwerk Plausec G.M.B.H. (British 361,363 [1930])
WC or W_2C		Fe, Co, Ni, W, Cr	A. Gronwall (British 380,941 [1931])
Tungsten Carbide		9% Mn	British Thomson Houston Co.; F. G. Kelley (British 355,041 [1930])

Initial Material	Carbon (%)	Additional Material	Patent
Tungsten Carbide up to 13%		Fe, Co, Ni, and Cu	Compagnie Française pour L'Exploitation des Procédés Thomson Houston (French 38,878 [1930])
WO_3 + C		Co (as solution of Co-Acetate)	Compagnie Francaise pour L'Exploitation des Procédés Thomson Houston (French 38,897 [1930]), Allgemeine Elektrizitats-Gesellschaft (German 555,786 [1930])
W + C or B		If necessary, Ta, Nb, Mo and 3 to 15% Fe, Co, Ni	Fansteel Products Co. Inc. (French 713,086 [1931])
Tungsten Carbide + Borocarbide or W + C + B		MoC, VC, TiC, ZrC, HfC, SiC and Co, Ni, Fe, Cr	F. Krupp Akt.-Ges. (French 716,597 [1931])
Tungsten Carbide	3 to 7	Up to 20% Fe, Co, Ni and 0.1 to 30% VC, NbC, TaC	F. Krupp Akt.-Ges. (French 718,697 [1931])
	2. *Sintering above Atmospheric Pressure*		
W	More than 3	Up to 0.1% B, up to 1.5% Si	O. Diener (British 294,086 [1928])
Tungsten Carbide or W + C		Silicide, Boride, Al_2O_3	O. Diener (German 504,484 [1926])
Tungsten Carbide		Up to 25% Fe, Co, Ni, Cu	Allgemeine Elektrizitats - Gesellschaft, General Electric Co.; S. L. Hoyt (Hungary 97,051 [1928])
W + C		Up to 25% Fe, Co, Ni, Cu	Allgemeine Elektrizitats - Gesellschaft; General Electric Co.; E. G. Gilson Colonie (Hungary 98,262 [1928]; 97,051 [1928])
W + C		Co	General Electric Co.; F. C. Kelley (U. S. 1,794,300 [1928])
Tungsten Carbide or W and a Hydrocarbon		Fe, Ni, Co	General Electric Co.; E. G. Gilson (U. S. 1,756,857 [1927]) Compagnie Française pour L'Exploitation des Procédés Thomson Houston (French 654,210 [1928])
W + C	3 to 7	5% Co	S. L. Hoyt (Japan 79,188 [1928])
W + C		Low melting metals	F. Krupp Akt.-Ges. (British 310,876 [1929]; Swiss 139,881 1929])

95 parts W		5 parts Borocarbide, 15 parts Co	General Electric Co.; S. L. Hoyt (U. S. 1,803,189 [1929])
Tungsten Carbide		U	Compagnie Francaise pour L'Exploitation des Procedes Thomson Houston (French 698,333 [1930]
80 to 97% Tungsten Carbide		3 to 30% Co	British Thomson Houston Co.; S. L. Hoyt, (British 360,709 [1930])
30 to 70% W		30 to 70% TaC, VC, NbC	Vanadium Alloys Steel Co., Ph. M. McKenna (U. S. 1,848,899 [1930])
93.8 to 95% W (+ C or B)	5 to 6.2	3 to 15% Fe, Co, Ni	Fansteel Products Co. Inc. (French 713,087 [1931])
Tungsten Carbide		Co or Co + W	G. J. Dillon, L. P. Malkow (Russ. 23,620 [1930])

III. Unspecified Processes

72% W + C or P		27.5% Al, Sn, Sb, Zn, Ni, Mg, Pb, Zr, Mn	P. R. Mallory Co.; G. N. Sieger, I. A. Weiger (U.S. 1,848,437 [1925])
50 to 72% W (+C)	Up to 3	27 to 50% Ag, Au or metal of the Pt-group	P. R. Mallory Co.; G. N. Sieger, I. A. Weiger (U.S. 1,848,458 [1925])
Graphite-free WC		Fe, Co, Ni	F. Krupp Akt.-Ges. (British 278,955 [1927]; Austria 111,835 [1927])
5 to 8% W	0.5 to 4	Up to 20% Mo, 0.5 to 20% Co, U, Zr, V, Ti, Si. Mo can be wholly replaced by Ta, while W only partly.	A. Kropf (British 264,528 [1927]; Swiss 127,586 [1927])
10 to 60% W	0.5 to 4	1 to 40% Cr, 1 to 40% Ta, 5 to 30% Mo or Ta or both. If necessary, Ni, Cr, Mn, V, Ti, Zr, U, Si	A. Kropf (British 270,640 [1927]; 264,528 [1927])
46 to 64% W	1 to 4	10 to 33% Fe, 11.5 to 16% Cr, 5.5 to 8% Co. Up to 4% Si, B, Zr, Ti, N, V, Be, Co. Up to 25% of W can be replaced by Mo, and Co by Ni	Hirsch, Kupfer-und Messingwerke A.G.; Karl Prinz zu Lowenstein, W. Muller (U.S. 1,847,617 [1928])
Tungsten Carbide		Up to 25% Co, up to 3% Th	General Electric Co.; L. Wyman (U. S. 1,822,720 [1929])
Tungsten Carbide		Electrolytically deposited Fe, Co, Ni, Cr	A. Hasselbach (French 701,944 [1930])

Some of the recent U. S. patents, pertaining to the manufacture of tungsten carbide are as follows:

1,803,276; 1,811,068; 1,840,457; 1,864,567; 1,893,078; 1,895,364;
1,895,959; 1,904,100; 1,904,568; 1,910,532; 1,910,804; 1,910,884
1,918,064; 1,925,910; 1,928,453; 1,932,499; 1,936,435; 1,940,308;
1,947,206; 1,959,879; 1,960,055; 1,961,468; 1,971,804; 1,973,422;
1,973,428; 1,973,441; 1,981,719; 1,982,857; 1,991,912; 1,998,609;
2,015,536; 2,018,752; 2,023,413; 2,026,958; 2,031,049; 2,033,513;
2,049,317; 2,053,151; 2,053,977; 2,057,786; 2,058,110; 2,074,847;
2,075,742; 2,082,354; 2,084,349; 2,091,017; 2,091,903; 2,093,844–5;
2,107,122; 2,113,353–6; 2,119,487–9; 2,122,157; 2,123,046; 2,123,574–6;
2,124,509; 2,128,146; 2,133,867; 2,134,305; 2,167,544; 2,171,391;
2,193,413; 2,196,009; 2,202,821; 2,207,708; 2,244,052–3;

German Cemented Carbide Industry

The following is taken from an article by Gregory Comstock (*The Iron Age*, pp. 36A–36L, Aug. 30, 1945).

Composition and Physical Properties of Standard German Cemented Carbides

Mark	Composition	Sintering Temperature °C	Duration of Sintering Temperature, Min Thickness of Tips		Bending Strength kg per sq mm	Elasticity Coefficient kg per sq mm	Heat Expansion number 10^{-6} cm Cm per °C	Heat Conductivity calories per sec per °C	Specific Heat	Electric Resistance
			2 mm	15 mm						
S1	78 WC. 16 TiC 6 Co	1600	20	100	125	54,000	6	0.09	0.06	0.43
S2	78 WC ... 14 TiC 8 Co	1550	20	100	140	—	6.2	0.08	—	0.44
S3	88 WC..... 5 TiC 7 Co	1500	20	100	150	59,000	5.5	0.15	0.05	0.25
G1	94 WC ... 6 Co	1420	20	100	160	62,000	5	0.19	0.05	0.2
G2	89 WC..... 11 Co	1400	20	100	180	58,000	5.5	0.16	0.05	0.18
G3	85 WC...... 15 Co	1380	17	60	205	—	—	—	—	—
H1	94 WC...... 6 Co	1420	17	60	160	64,000	5	0.19	0.05	0.21
H2	91.5 WC.... 0.5 VC 1 TaC 7 Co	1500	66	220	115	—	5	—	—	0.25
F1	69 WC...... 25 TiC 6 Co	1550	66	220	110	52,000	7	0.05	—	0.65
F2	34.5 WC.... 60 TiC 5.5 Co	1700	66	200	80	—	—	—	—	0.77

Representative Analysis of German Cemented Carbides Produced During the War

Grade S1

C	
ges	7.57
frei	(0.21)
W	73.33
Co	5.48
Ti	12.76
Fe	0.31
Cr	0.03
Ni	0.10
N2	0.26
Spez. Gew	11.15
Harte	91.0

Grade S2

C	
ges	7.30
frei	(0.22)
W	73.06
Co	7.64
Ti	11.13
Fe	0.28
Cr	0.05
Ni	0.11
N2	0.29
Spez. Gew	11.25
Harte	90.5

Grade S3

C	
ges	6.17
frei	(0.16)
W	82.55
Co	6.63
Ti	3.77
Fe	0.25
Cr	0.05
Ni	0.09
N2	0.15
Spez. Gew	13.30
Harte	90.0

Grade G1

C	
ges	5.90
frei	(0.15)
W	87.75
Co	5.68
Fe	0.34
Cr	0.09
Ni	0.10
N2	0.06
Spez. Gew	14.70
Harte	90.0

Grade G2

C	
ges	5.65
frei	(0.18)
W	83.22
Co	10.46
Fe	0.38
Cr	0.05
Ni	0.12
N2	0.03
Spez. Gew	14.20
Harte	88.5

Grade G3

C	
ges	5.50
frei	(0.32)
W	79.32
Co	14.46
Fe	0.40
Cr	0.06
Ni	0.10
N2	0.03
Spez. Gew	13.70
Harte	87.0

Grade H1

C	
ges	5.83.
frei	(0.12)
W	87.82
Co	5.66
Fe	0.30
Cr	0.05
Ni	0.11
N2	0.03
Spez. Gew	14.75
Harte	91.0

Grade H2

C	
ges	5.83
frei	(0.16)
W	85.14
Co	6.80
Fe	0.28
Cr	0.06
Ni	0.11
Ta	0.77
V	0.5
Nb	0.20
N2	0.03
Spez. Gew	14.40
Harte	91.5

Grade F1

C	
ges	8.10
frei	(0.06)
W	66.86
Co	5.48
Ti	18.30
Fe	0.40
Cr	0.13
Ni	0.15
N2	0.42
Spez. Gew	9.90
Harte	91.5

Grade F2

C	
ges	12.8
frei	(0.05)
W	32.40
Co	5.25
Ti	46.60
Fe	0.71
Ni	0.14
Cr	0.10
N2	1.14
Spez. Gew	6.8
Harte	92.5

Grades *S1*, *S2*, *S3* and *F1*, *F2* are primarily designed for steel cutting. The *G* and *H* grades are for case iron, nonferrous metals and alloys and other materials. *S1*, *S2*, and *S3* are of progressively increasing strength and decreasing hardness as are the series *G1*, *G2* and *G3*. Grades *H1* and *H2* are carefully developed special grades. *H1* is of almost the same calculated composition as *G1* and the same strength but is materially harder. It is sintered for a shorter time and has a finer ultimate grain size. Grade *H2* contains small quantities of vanadium and tantalum carbides, is the hardest standard grade produced, and is employed in the machining of extremely hard materials.

Consideration of the composition of these materials, their reported physical characteristics and their recommended applications would seem to indicate an extremely well chosen group of hard cemented carbides for wide application to general industrial usage. The use of tantalum or columbium as carbide additives to hard metal has always been discouraged in Germany, possibly because of the difficulties attendant to their consistent procurement. German war research reports secured during the investigation showed a marked tendency toward the use of columbium in small but significant percentages.

In German practice, machining grades of hard carbide are recommended on the basis of the material to be cut, *i.e.* ferrous and nonferrous, nonmetallic, etc.; the amount of material to be removed, *i.e.* depth of cut at high, medium or low speeds; the strength of cutting characteristics of the materials to be machined; the type of operation, *i.e.* turning, milling, boring, etc., and special considerations such as finish. On this basis grade *S1* is recommended for general steel cutting, although comparatively light cuts at high speed are specified and applications are limited to machine tools capable of taking full advantage of carbide cutting efficiency. This grade is the most generally employed of all of the German hard carbide products.

Grade *S2* is for heavier steel cutting than grade *S1* with permissible increases in depth of cut up to 30 per cent of those recommended for *S1*. *S3* is recommended for still heavier cuts, for intermittent machining operations and for use in old machine machine tools. Grade *G1* is the original Schröeter composition refined by production experience and research. It is recommended for the machining of cast iron, copper, the light metals and a variety of other materials. It is used in quantities second only to Grade *S1*.

G2 and *G3* are recommended for progressively heavier cuts of the *G1* type, for operations involving increasing resistance tò shock or impact. The *F* types were developed for such special uses as the boring of aircraft cylinders or other similar applications where light cuts of long duration and extremely fine tolerances are involved which permit of little or no tool-end wear (*F1*). Another example cited of the advantageous use of these grades is the close tolerance machining of from 500 to 700 connecting rods per grind, using *F1*. *H* grades are recommended for the machining of either naturally hard alloys or those in the hardened state as a result of heat treatment. For surfacing or shaping operations, *S* grades are recommended for steel, *G* grades for iron and a variety of other crisp cutting materials.

Reporting on the most notable improvements in the manufacture of hard cemented carbides over the last twelve years, technical executives of the Hartmetallezentralle list the following:

"Before 1936 the mixing of metallic tungsten powder with sugar carbon or graphite was done in 8-liter drums. After that time, ball mills made by Messrs. Rohrbach with a diameter of 150 mm and a length of 250 mm were employed which permitted mixing charges of 250 kg.

"The mixture of tungsten and carbon was originally tamped into carbon boats previous to carburization. Since 1939 this mixture has been pressed into briquettes in hydraulic presses under conditions giving them sufficient green strength to be handled. They are then inserted in this compressed form into graphite containers. This method saves labor and has the further advantage of affording better carburizing and an increase production per furnace has been made possible.

"Before 1931 carburizing was accomplished in gas-fired furnaces. Electric furnaces were employed after that date. These furnaces are of the graphite tube-resistance type. The length of carburizing furnaces has been increased from the original 930 mm to 2000 mm in the course of the last few years. This increase in the length of the uniformally heated high temperature zone permits a higher stoking rate and the output per furnace has been tripled.

"The crushing of the carbide cake previous to 1938 was a hand operation. Since that time the cake has been broken into coarse chunks in jaw crushers and reduced to fine powder in impact mills.

"In order to increase the output of the Essen works, a 175-liter milling mechanism was put into operation instead of those of 8-liter capacity used up to 1940. The charge of carbide plus binder metal in these machines is now 250 kg. Another marked improvement was the introduction of the oscillating or vibrating mill for the grinding of graphite or sugar carbon as well as the grinding of carbide plus binder. This was done in 1939 and 1940. The milling time in this type of mill is only a fraction of that required for the standard rotating ball mill. The milling time in the oscillating mill is one-sixth of the time required in the standard ball mill when charges of carbide plus binder are treated. Graphite or sugar carbon is pulverized in these mills with porcelain balls. Steel balls are used for blending tungsten and carbon in this mill and hard carbide balls are employed for grinding tungsten carbide plus metal binder. In 175-liter mills, 300 to 500 kg of hard cemented carbide balls of 25 and 40 mm diam are used. The hard cemented carbide balls are hot pressed.

"In 1941 a new system was installed for drying the wet-ground carbide plus binder mixture. This consists of applying a low vacuum to the mills when they are immersed in a water bath heated to 80°. This removes practically all water in a relatively short time and does not involve the use of hydrogen. The vacuum-dried powder is, however, rapidly reduced at 600° by stoking it through multiple tube hydrogen furnaces.

"Previously the mixed powders ready for pressing were moistened in small quantities with a sprayer and then mixed by hand. After 1938 this operation was performed in a mixing machine of 10 kg capacity. As a moistening agent, Krupp has recently used acetone or glycol or methyl alcohol as well as the old solution of camphor and benzene (70 g of camphor to 1 liter of benzene; 350 cu mm of this solution used for 10 kg of the pressing mixture). Glycol was particularly successful as a moistening agent.

"The pressure required for titanium grades is 50 to 100 kg per sq cm. For *G* grades, 80 to 120 kg per sq cm, and for *H1* and *H2* 100 to 120 kg per sq cm. For these latter grades the pressure has to be higher because the height of these mixtures as poured into molds is greater than that of the *G* grades and, therefore, higher pressure becomes necessary if the compressed product is to have the same weight size ratio as the *G* types.

"With the advent of standardized tips, improvements were possible in their pressing. The German practice is to press in hand-powered presses one tip at a time, which is much faster than might be expected. In one of the plants 200,000 tips per month were produced from prepared powders with approximately 30 employees engaged in all operations.

"In 1940 a major change in the methods of producing tungsten carbide plus titanium carbide compositions was effected (grades *S1* and *S2*). Originally tungsten carbide, titanium carbide and cobalt or nickel powders were wet ground, dried, lubricated and subsequently pressed and sintered. The method employed at Reutte of heating the mixed carburized powders to high temperature was thoroughly investigated. It was found that a more homogeneous mixture was obtained and a possible improvement in the control of crystal growth was noted. In the manufacture of Grades *S1* and *S2*, mixtures of tungsten carbide, titanic acid and carbon are heated to 1700° as a substitute for the Reutte process. The temperature required for most efficiently carburizing titanium carbide (in the German practice) is in the neighborhood of 2300°. The advantages of this innovation are the elimination of previous milling operations applied to the individual carbides; the use of lower temperatures which greatly prolongs the life of the furnace; increased homogeneity and control of ultimate particular size; and increased production per unit of milling and furnace equipment.

"A composition change was made in grades *S2* and *S3* in order to increase the differences in physical characteristics between them and thereby permit a broader spread of application. The titanium carbide content of *S2* was lowered by 2 per cent and the cobalt content of grade *S3* was increased from 6 to 7 per cent.

"Krupp special grade *H167* (later classified as Deutsches Hartmetalle *H2*) was developed in 1938 for the machining of chilled molds of over 90 Shore hardness. In the same year, grade *F1* was produced for the fast finishing of steel. During the war, grade *F2* was developed to permit a further increase in cutting speed over that made possible by grade *F1*.

"The possibility that stocks of tungsten available for hard cemented carbide might be exhausted should the war be indefinitely prolonged induced concentrated research at the beginning of the war for a tungsten-free hard carbide cutting material. The experiments were successful and culminated in a titanium carbide—vanadium carbide substitute for *S1*. Tool tips of this material have for some time been used in mass production factories under conditions where grade *S1* tips were previously employed. This grade is called *V814* and its composition is 45 per cent titanium carbide, 45 per cent vanadium carbide and 10 per cent nickel or 7 per cent nickel and 3 per cent cobalt. It is generally hot pressed although it can be made by the cold press vacuum sintering method."

Seven years of consistently good engineering have brought the metal powder hot press to a high state of perfection in Germany. It was found in use as an efficient hard carbide production implement. One of the chief difficulties experienced in the past with this device was associated with its excessive use of graphite die and plunger forms. The German engineers have bypassed this disadvantage by pressing thin walled cylinders of other tube forms broached from graphite into heavier graphite mold containers. These units are replaced after use with a minimum discard of reclaimable graphite. Plungers are remachined to original contours by form cutters with little loss of either time or material. In order to minimize plunger movement during pressing, the carbide plus binder powders are pressed into temporarily reinforced graphite molds under heavy hydraulic pressure previous to hot pressing.

The German hot press is of the graphite resistance type, the spring clamped mold being the resistor with a separate mechanical or hydraulic system available for applying top and bottom plunger pressure. A corps of expert electrical, mechanical and metallurgical engineers have followed this hot press development to a conclusion and have been successful in designing a most ingenious series of auxiliary machines for the mass production of mold, plunger and separator forms and for the grinding and finishing of the product. The result has been a system of hot pressing rather than the improvement of the hot press as a unit device.

The advantages of employing the hot press as a means of quickly and inexpensively producing very large objects of hard cemented carbide or of a limited number of pieces of intricate cross-section have been recognized in the U. S. for a long time. These assets have been carefully retained in the German practice. One of the difficulties associated with the simultaneous application of great heat and even relatively low pressure has been the loss of the molten binder by extrusion. The Germans report that they have in a measure overcome this by controlling the final volume of carefully weighed prepressed charges having a constant apparent density. A consistent and controllable binder loss on the order of 2 pct is mentioned for hard carbide compositions having originally as much as 13 pct of the auxiliary metal. The production cycle of this system is calculated to produce a finished hot pressed mold charge in from 3 to 7 min for pieces from 50 to 1000 g in weight. Larger objects, of course, require a longer time. As many as 19–200 to 300-g pieces have been pressed in one mold in production quantities. It would seem that while the German hard carbide industry has apparently nothing comparable to the new American cold extrusion process, they have made a most notable improvement on hot pressing apparatus and technique. This system certainly merits close Allied study and further extensive investigation both at home and in Germany.

Commenting on the German Cemented Carbide industry during the War, Philip M. McKenna makes the following observations (*The Iron Age*, pp. 65–68, Feb. 7, 1946).

Apparently under Nazi rule fundamental progress had stopped, because the cemented-carbide products disclosed are in the same stage of development as they had been 10 years ago in the United States.

There were as many machine tools in Germany today, in reparable condition, as there are in the whole United States. Yet they point out that American industry produced three or four times as great an output of arms and munitions, and the question is raised as to how was this possilbe. Certainly one of the obvious answers is that the possession of cemented hard-carbide tools having 30 to 50 per cent higher break-strength in America was a chief reason. This is because the higher resistance to breakage of American steel-cutting carbide tools permitted feeds per revolution three to four times those possible with German grades for steel cutting.

Records of shell production show that it is a conservative statement to say that 1 gm of steel-cutting cemented carbide having 50 per cent higher break strength when of equal hardness turns out 4.3 times as many shells as cemented carbides of the German characteristics.

German vs. American Cemented

Grade Designation Symbol	Transverse Rupture kg per sq mm	Equivalent in psi	Equivalent on Standard Blanks kg to break	Ra Hardness	Tool Value* Computed	Notes
German Steel-Cutting Grades						
S1	125	177,900	1430	91	92	78 WC, 16 TiC, 6 Co
S2	140	199,220	1526	90.5	94	78 WC, 14 TiC, 8 Co
S3	150	213,500	1720	90.0	101	88 WC, 5 TiC, 7 Co
Steel-Cutting Grades of One American Manufacturer						
K4H	157	225,000	1720	92.3	122	Having $WTiC_2$ as an ingredient
K3H	183	260,000	2090	92.0	179	Greatest percentage of $WTiC_2$
KM	214	305,000	2460	91.0	159	Having medium content of $WTiC_2$
K2S	214	305,000	2460	91.5	164	Having $WTiC_2$ as an ingredient
German Cast-Iron Cutting Grades						
G1	160	227,680	1830	90.0	108	94 pct WC, 6 pct Co
G2	180	256,000	2060	88.5	101	89 pct WC, 11 pct Co
G3	205	291,715	2350	87.0	96	85 pct WC, 15 pct Co
H1	160	227,680	1840	91.0	118	94 pct WC, 6 pct Co (Doubtless selected grain size)
Cast-Iron Cutting Grades of One American Manufacturer						
K6	157	225,000	1800	92.2	125	WC and Co with grain-size control
K12	246	350,000	2800	89	147	WC and Co with grain-size control

To convert kg per sq mm to psi: multiply by 1423. kg of load to break standard piece × 124 = psi: transverse rupture.

$$\text{*Tool value} = \frac{10 \times \text{break strength in kg.}}{\frac{5\,(93\text{-Ra})\,(47\text{-Ra}) + 140}{2}}.$$

MANUFACTURE OF FERRO-TUNGSTEN

Most of tungsten ores now produced go into the manufacture of ferro-tungsten. The Alumino-thermic, the Silico-thermic and the Crucible methods have been proposed for the manufacture of ferro-tungsten; but the direct reduction of tungsten ores in the electric furnace is the common process now adopted for the production of ferro-tungsten.

Reduction with Carbon in Crucibles.

Most of the ferro-tungsten was made in crucibles until the introduction of the electric furnace about 1900. The tungsten concentrate is placed in a clay-lined crucible with the proper proportion of coke or charcoal flux and tool-steel scrap and the whole is heated in a gas-fired furnace. For a 30 per cent tungsten alloy a crucible will last about three heats, but for a 65 to 75 per cent product, it will last but one heat.

The Alumino-thermic Method. Rossi[63] reduced ferberite (WO_3 69.86 per cent, SiO_2 5.04 per cent, FeO 20.25 per cent) with aluminum in a Siemens type electric furnace and obtained an alloy containing 75.91 per cent tungsten, 21.47 per cent iron, 1.61 per cent silicon, 0.08 per cent sulfur and 0.9 per cent carbon.

The gangue of the ore can be slagged off by using fluxes such as lime, soda ash, fluorspar, borax etc. in conjunction with the alumina resulting from the reaction. To effect the reaction speed, the aluminum used is between 8 and 30 mesh (1.5 and 0.6 mm diameter). The most advantageous particle size of the ore charged seems to be between 0.05 and 0.25 in (1.3 and 6.4 mm).

Tungsten oxide or tungsten concentrate may be reduced with aluminum powder in a magnesia crucible, with an ignition mixture of sodium or barium peroxide and aluminum powder. The product formed is always free from carbon, but may contain aluminum and other reducible metals such as copper, manganese, etc. which may be present in the ore.

It is reported that this process has been adopted in England.

The Silico-thermic Method. Gin[64] has produced ferro-tungsten by using an electric furnace with two contiguous hearths in series, having ferrosilicon electrodes and an intermediate electrode formed by a bath of ferrosilicon. Scheelite is placed upon the melted bath of ferro-silicon when the following reaction takes place:

With 20 per cent ferro-silicon:

$$3CaWO_4 + 4Fe_2Si \rightarrow (2Fe_2W + Fe_3W) + 3CaSiO_3 + FeSiO_3$$

With 33 per cent ferro-silicon:

$$3CaWO_4 + 4FeSi \rightarrow 3FeW + 3CaSiO_3 + FeSiO_3$$

With 50 per cent ferro-silicon:

$$3CaWO_4 + 2FeSi_2 \rightarrow FeW_3 + 3CaSiO_3 + FeSiO_3$$

The Metallothermal Process[65], as developed by Yelyutin, is in fact a combination of the Alumino-thermic Method and the Silico-thermic Method and may prove to be practical. With this process, the reduction of the ore for the production of ferro-tungsten is realized without the application of electric furnaces, that is, without any application of heat from the outside. For the purpose of smelting (ignition), a special knock-down hearth is built, with lining of magnesite brick or rammed magnesite.

As an experiment, the charge was composed of the following: 22 lbs tungstite, 2.4 lbs ferrosilicon, 3.1 lbs aluminum, 2.2 lbs spar, and 4.4 lbs mill scale. Before smelting, all these materials were thoroughly intermingled, after which part of the charge was thrown upon the hearth. To start the reducing reaction, a small quantity of an ignition mixture consisting of BaO_2 and ferro-silicon was strewn upon the charge on the hearth. While this mixture underwent combustion, the temperature of the initial reaction was reached in part of the charge. After combustion of the starting mixture, the reducing reaction began in the main body. As the reaction developed, new portions of the charging materials were added. The entire process of reduction, as a rule, was completed within from 3 to 5 minutes. After the slag had solidified, the hearth was broken up and the finished block of ferro-tungsten was removed.

In this manner, a ferro-tungsten was obtained with 72–82 per cent W, 0.3–1 per cent Si, 0.2–2 per cent Mn, and 0.1–0.2 per cent C.

When igniting charges containing 66 lbs wolframite and corresponding quantities of the other components, the ferro-alloy obtained has the following composition: 0.115 per cent Si, 0.23 per cent Mn, and 0.44 per cent Al. The alloy obtained was found to be completely free from slag-like impurities, and the slag did not contain any reguli of metal. The yield of tungsten in the ferro-alloy was as high as 93 per cent (without collection of the gases and the dust). To obtain 1 lb of tungsten in the alloy, there were required, on the average, 2.275 lbs wolframite, 0.245 lb ferro-silicon, 0.290 lb aluminum, 0.319 lb scale, and 0.218 lb fluorspar.

The metallothermic reduction method as practiced at the Climax Molybdenum Co. for the manufacture of ferro-molybdenum may be adopted for the manufacture of ferro-tungsten. The furnace, consisting of a cylindrical steel shell, lined with Carboflex, that is, a silicon carbide brick, has the following dimensions: external diameter 60 inches, internal diameter 52 inches, and height 44 inches. The furnace can be lifted by an overhead travelling crane as soon as reaction is completed. The ferro button rests on the sand bed while the slag flows into a slag pond. The ignition charge consists of a few ounces of aluminum and sodium peroxide.

Reduction in Electric Furnaces.

As the melting point of commercial grades of ferro-tungsten (75–80 per cent W) is comparatively high, it has so far been found impractical to smelt ferro-tungsten in the same way that ferro-silicon and ferro-manganese are smelted. Hence ferro-tungsten is produced discontinuously, that is, in knock-down furnaces.

The following description of the manufacture of ferro-tungsten in two stages has been given by Keeney[66]:

"One method commonly employed for production of ferro-tungsten is reduction of ferberite or some other concentrate in the electric furnace, with carbon as a reducing agent, followed by a subsequent refining and decarburization. Reduction with carbon takes place according to the following reaction:

$$FeWO_4 + 4C \rightarrow FeW + 4CO$$

"Theoretically the product would contain 76.6 per cent tungsten. The slag may contain as high as 8 per cent FeO, but less than 1 per cent WO_3. Theoretically the reduction of 100 parts of alloy from 126 parts of ferberite requires 20 parts of carbon, but practically about 25 per cent excess of carbon is charged. Small amounts of lime and fluorspar are used to flux the silica. Operating in this manner with an excess of carbon a product is made containing 3 per cent carbon, 70 per cent tungsten, 0.05 per cent phosphorus, and 0.01 per cent sulfur; the slag contains below 1 per cent WO_3. If desired, this product can be tapped from the furnace, but as its behavior is erratic, it is preferable to allow the metal to collect in the bottom of the furnace, forming, in a 150-kw furnace (at 95 volts), a button about 3 feet in diameter, 6 inches thick, and weighing 1,000 to 1,200 pounds; the slag is poured off by tilting as it fills the furnace.

"Smelting of ferberite concentrate. A typical operation is conducted as follows: The initial charge is 65 pounds of a mixture composed of 200 pounds concentrate, 42 pounds coke, 56 pounds lime, 6 pounds fluorspar. Three more 65-pound charges are added at intervals of half an hour, and at 2½ hours from the start the furnace is tilted and the slag poured. This cycle is repeated until a 1,200-pound button has been formed, requiring 24 to 36 hours. The furnace is allowed to cool, is torn down, and the button of metal removed. This is then cleaned and broken up, the breaking process being somewhat difficult with a 3 per cent carbon alloy.

"The slags produced average 0.72 per cent tungsten, and though there is considerable mechanical loss, due principally to dusting, the total loss in practice does not exceed 5 per cent.

"*Refining ferro-tungsten.* The crude metal, broken to about 6-inch size, is refined as follows: A charge of 150-pound metal and 75-pound ferberite concentrate is smelted for half an hour, when 12 pounds of fluorspar is added. After another 3 hours the slag is poured, and a fresh charge is started. The process is continued for from 36 to 48 hours, until a button weighing 1,500 pounds has formed in the furnace, a larger button being permissible because the low-carbon alloy is easier to break. The furnace is allowed to cool, is torn down, and the button of metal removed, cleaned, and broken. The refined button forms compactly and is free from slag. The refining reduces the carbon from 3 to 0.8 per cent, the phosphorus from 0.05 to 0.01 per cent, leaves the sulfur the same, and increases the tungsten from 70 to 75 per cent. The refining slag contains 5 to 20 per cent tungsten, and is resmelted in a special run.

"Nearly every manufacturer of ferro-tungsten has tried to tap it from the furnace, but none has continued the practice. If the tungsten is reduced to 55 to 60 per cent, the alloy can be tapped, even with carbon as low as 0.2 per cent. With tungsten at 70 per cent, metal containing 0.9 per cent carbon has run out while pouring slag, but generally any metal which comes out with the slag will contain 1.25 per cent carbon. The irregularity of tapping operations with ferro-tungsten has prevented the adoption of that method, because if part of the metal must be retained in the furnace, it is cheaper to keep it all there."

The manufacture of ferro-tungsten in the electric furnace in a single operation, as distinguished from the two-stage operation, has been described by Dailey[67]:

"The following is a representative furnace mix:

Typical Analysis of a Low Manganese Bolivian Wolframite

	(per cent)
Tungstic oxide	69.75
Ferro oxide (FeO)	23.29
Manganous oxide	0.83
Lime (CaO)	1.06
Silica	3.45
Sulfur	0.125
Phosphorus	0.031
Copper	0.05
Tin	0.16
W:Fe ratio	75.48
	95.75

"The above ore had been roasted to eliminate sulfur and, frequently, arsenic. The analysis represents roasted ore.

Furnace Charge for This Ore:

	(pounds)
Ore	300
Coke, 90% fixed carbon	40
HS scale, 60% iron	—
Furnace trimmings	40
Sand, 95% SiO_2	—
Lime, 63% CaO	5
Fluorspar	5
Common salt (NaCl)	3
	393

Typical Analysis of Slag:

	(per cent)
Tungstic oxide	0.44
Ferrous oxide	11.21
Manganous oxide	3.02
Lime	18.72
Silica	44.54
Alumina	20.79
Sulfur	0.38
	99.10

"The high alumina content is derived from the furnace trimmings going into these low manganese charges. A varying amount of this intermediate is gotten when the furnaces are torn down. It is largely the furnace brick that has come into contact with the tungsten-bearing charge and carries, consequently, too much tungsten to warrant its being discarded. It is disposed of and kept from accumulating by mixing it with the ore charge. Such an intermediate varies greatly in tungsten content. It may assay from 3 to 8 per cent tungsten.

A typical analysis of the ferro-tungsten resulting from one-stage smelting operation is as follows:

	per cent
Tungsten	75.73
Carbon	0.47
Sulfur	0.037
Phosphorus	0.038
Silicon	0.48
Manganese	0.56
Lime	0.10

"Varying amounts of Reclamation Material 'B' product result from the breaking up of each button. Ideal heat conditions, during the run, minimize the amount of this product with a corresponding increase in the quantity of marketable ferro-tungsten, but as the furnaces are hand-operated with respect to the raising and lowering of the carbon electrodes over the 24 hours of the day (three eight-hour shifts), the changing of crews and work of different metermen introduces widely varying human factors which are reflected in the make-up of the resulting buttons.

"This Reclamation Material 'B' is not marketable as such, so must be treated to get its high tungsten content into marketable ferro-tungsten.

"A typical Reclamation Material 'B' intermediate analyses as follows:

	per cent
Tungsten	48.85
Iron	19.31
Carbon	1.53
Sulfur	0.115
W:Fe ratio equals ferro of	71.67

"To make ferro-tungsten containing 75 per cent tungsten and of acceptable carbon content (0.50 to 0.60 per cent C) from this intermediate the tungsten-iron ratio must be raised and the carbon content lowered. Obviously this can be accomplished in several ways. The use of tungstic oxide and tungsten ore for this purpose readily suggest themselves. Both these expedients work out satisfactorily.

"In the practice under discussion, we have normally pursued a somewhat different course. It has been found out that this type of intermediate, when finely ground (10 mesh or finer in Lehigh Fuller mills or Sturtevant ring rolls) suffers oxidation if moistened and exposed to the air. This oxidation is hastened by stirring the finely ground, moistened material in any heavy-duty mixer such as one of the Werner-Pfliederer type. Ten minutes of such stirring or mixing, keeping the material just damp, suffices to bring about oxidation that heats up the product to a temperature at which the hand cannot be kept in contact with it. Clouds of vapor arise; they have an odor of hydrocarbons, but repeated tests before and after such 'rusting' process, have failed to evidence any commensurate loss in carbon content. The carbon remaining in the 'rusted' material is sufficient to reduce again such tungsten as may have been oxidized by 'rusting', but the greater part of the iron oxidized at the same time passes into the slag upon smelting. In this manner, the tungsten-iron ratio is increased to the point desired and the carbon correspondingly lowered.

"A typical mix for furnace charges of a 'rusted' product such as has just been described, would be the following:

	pounds
Reclamation material B	400
Furnace trimmings	40
Common salt (NaCl)	4
	444

Such mixes may be used in combination with ore charges, or they may constitute the sole charge going into the furnaces. In the latter case, obviously, the duration of the furnace run would be considerably under the 30 hours allotted for ore runs, as such a charge would be materially richer in tungsten, would require melting only, and would make ferro-tungsten much faster, thus filling the furnaces in a much shorter time.

"In general, the advantages of making acid electric furnace ferro-tungsten are: Higher recoveries because of the lessened tendency of tungsten to go into a slag of high silica content as compared to its tendency to enter readily basic slags high in lime; production of a ferro-tungsten practically free of lime. The principal and only practical disadvantage is that ores must be more nearly 'dead-roasted' to free them of sulfur and arsenic than should be necessary under more basic conditions where the lime can be depended upon to slag off greater amounts of these elements than would thus be removed by siliceous slags.

"Incidentally, a very efficient roasting practice was developed as a result in which tungsten ores with sulfur in excess of 4 per cent and arsenic correspondingly high could be roasted to a sulphur content of 0.10 per cent or less, with a tungsten loss of appreciably less than 1 per cent. Gas was used in a rotary inclined roaster. It was automatically hopper-fed with a ten-mesh product, or at times a four-mesh product, depending upon the character of the ore. This roaster had a capacity of from 300 to 500 pounds of practically dead-roasted ore hourly.

"Summary: 1. Ferro-tungsten assaying 75 per cent tungsten and about 0.50 per cent carbon can be produced readily by one-stage smelting under conditions productive of acid slags.

"2. Tungsten recoveries in excess of 90 per cent are obtainable.

"3. Current consumption is about 1.62 kwh per pound of tungsten produced from low-manganese wolframites and 1.75 kwh per pound of tungsten produced from high-manganese hübnerites.

"4. Ores must be well roasted in order to insure a ferro-tungsten of low sulfur content.

"5. Resulting ferro-tungsten is practically lime-free."

It has been reported that the Ampere Co. of Berlin[68], smelted scheelite direct with sulfide of iron, with an addition of carbon in the electric furnace according to the following reaction:

$$CaWO_4 + FeS + 4C \rightarrow FeW + CaS + 4CO$$

Lime was added to flux the silica contained in the scheelite, resulting in the formation of a slag, in which is contained the calcium sulfide formed according to the above formula.

Present Method of Manufacture of Ferro-tungsten*

The first ferrotungsten produced in the United States in 1916–1918 was made in small, knock-down, fire-brick furnaces, using 4″ graphite electrodes and a power input of about 50 KVA. Furnace charges generally weighed 150 lbs; time of inditidual heats varied from 2 to 4 hours; and after a campaign of about 60 hours, the furnaces were knocked down, showing a button of ferrotungsten weighing 300-400 lbs. The yield at that time was about 70 per cent and the resulting ferro was divided into seven different products, only one of which was suitable for sale; the other six were remelted by various methods. The saleable portion constituted somewhat less than 50 per cent of the amount of tungsten charged.

The next step, which was at that time considered a revolutionary development, was the evolution to a furnace having a reduction area of about 4 sq ft. This furnace was simply a steel shell with a rammed lining of dolomite and pitch. The average charge to this furnace consisted of about 350 lbs. A campaign lasted three days and buttons of ferrotungsten weighing about 3000 lbs were produced. The yield in ferrotungsten was thus increased to 80 per cent, equivalent to about 65 per cent of the tungsten charged.

---

* Information from Mr. E. A. Lucas.

During the period from 1918 to 1928, this furnace remained standard. Yields, however, had increased to about 88 per cent, about 75 per cent of the tungsten charged being recovered in saleable form. Experimental work on furnace, linings, slag control, impurity elimination, etc., had been extensive; as a result, the cost of manufacture was cut about half and the quality of the product was improved.

In late 1929 and early 1930, the present type of reduction furnace was designed, and several units were built to study the effect on quality, costs, recovery, etc.

This type of furnace is approximately 60 in high and 54 in wide (see illustration) and has an active area of about 16 sq ft. With some changes in mechanical and electrical design, this same type is still in use today. Charges of 1500 lbs are average. A campaign lasts from 72 to 90 hours and the button of ferrotungsten weighs approximately 14,000 lbs. Yields are above 90 per cent and practically all the material produced is of saleable quality.

Electric furnaces for manufacture of ferrotungsten. *Courtesy Molybdenum Corp. of America.*

In operation either acid or basic practice is used, depending on the type, grade and quality of ores used. The charge consists of concentrates, lime, sand, coal, scrap, scale, materials recovered from slags, and such chemicals as are required to remove tin, copper, arsenic, etc. present in the mixture.

Satisfactory operation is obtained with wolframite, scheelite, ferberite, or hübnerite, separately or in combination, providing the iron-tungsten ratio is such that it will permit formation of an alloy containing 70 per cent or higher tungsten content. A usual combination is wolframite 70 per cent, scheelite 25 per cent and ferberite 5 per cent.

As a furnace fills and is ready to be worked, the steel shell is removed, lining material is chipped off, and the cleaned button is broken in a pit into pieces ranging in weight from 10 to 100 lbs. These are rough-crushed to about 2″ pieces, sorted and crushed to final size. Ferrotungsten is usually shipped in one of two sizes, either 1 in to $\frac{3}{8}$ in and $\frac{3}{8}$ in down. Crushed ferrotungsten of the 77-82 per cent grade, crushed to 1 in down, weighs about 475 lbs per cu ft.

References

General:

Alterthum, H., "Wolfram: Fortschritte in der Herstellung und Anwendung in den lezten Jahren", Braunschweig, Friedr. Vieweg & Sohn, 1925.

Friend, J. Newton, "A Text-Book of Inorganic Chemistry", Vol. **VII**, Part III, pp. 183–186 and pp. 201–204, London, Charles Griffin & Co., 1926.

Gmelin's, "Handbuch der Anorganischen Chemie", System-Number 43, Wolfram, pp. 19 40, Berlin, Verlag Chemie, 1933.

Knepper, F. von, "Die Fabrikation von Wolframdrahten fur elektrische Gluhlampen und Radiorohren", Verlag von Hachmeister & Thal in Leipzig.

Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. **XI**, pp. 682, 699.

Mennicke, "Die Metallurgie des Wolframs", Berlin, 1911 London, Longmans Green & Co , 1931.

Runner, J. J., and Hartmann, M. L., "The Occurrence, Chemistry, Metallurgy and Uses of Tungsten" Bull. No. 12, Dept. of Geology and Chemistry, South Dakota School of Mines, 1918

Smithells, Colin J., "Tungsten", pp. 9–121, New York, D. Van Nostrand Co , 1936.

Weber, C. Heinrich, "Die elektrischen Metallfadenglühlampen", pp 100–108, pp. 108–146, Leipzig, 1914.

Decomposition of Tungsten Ore:

1. Jones, C. H., "Manufacture of Pure Tungsten Metal; Operations at the Fansteel Products Company, *Chem. Met. Eng.*, **22,** 9 16 (Jan. 7, 1920)
2. Gordon, N. T., and Spring, A F., "Continuous Process for Manufacture of Sodium Tungstate and Tungstic Acid from Wolframite", *Ind. Eng. Chem.*, **16,** 555-562 (June, 1924).
3. Smithells, Colin J., "Tungsten", p. 10.
4. Malenitzski, I. N., "Autoclave Process of Tungsten Extraction from its Concentrates", *Tzvetnyye Metally*, **4-5,** 140-3 (1939).
5. Scheibler, C. J., *Pr. Ch* , **83,** 276 (1861).
6. Bernoulli, F. A., *Pogg. Ann.*, **111,** 589 (1860).
7. Zettnow, E., *Pogg. Ann.*, **130,** 16 (1867).
8. Bucholz, C. F., "*Schweigger's Journ.*", **3,** 1, 1811.
9. Gero, W. B., and Iredell, C. V., "Making Pure Tungstic Oxide Involves Many Unusual Plant Problems", *Chem. Met. Eng.*, **35,** 412-417 (July, 1928).
10. *Schweiggers J. Chem. Physick*, **16,** 476 (1816).
11. *Z. anorg. Ch.*, **65,** 300 (1910).
12. Gin, Gustave, "Memoir on the Methods of Treatment of Simple and Complex Ores of Molybdenum, Tungsten, Uranium, Vanadium", *Trans. Am. Electrochem. Soc.*, **XIII,** 501 502 (1908).
13. *Compt. Rend.*, **81,** 95 (1875).
14. *Zeit. Anorg. Chem.*, **65,** 302 (1910).
15. Private Communication.
16. Gin, Gustave, *Ibid.*, 500.
17. Gin, Gustave, *Ibid.*, 500-501.
18. Smithells, C. J., "Tungsten" p. 12, New York, D. Van Nostrand Co., 1936.

18.a Report of the Tin and Tungsten Research Board, Dept. of Scientific and Industrial Research, H. M. Stationary Office (1922), p. 62-64.

19. Gin, Gustave, *Ibid.*, 505.
20. Smithells, C. J., *Ibid.*, p. 14.

21. Alterthum, H., "Wolfram, Fortschritte in der Herstellung und Anwendung in den letzten Jahren, F. Vieweg & Sohn Akt.-Ges., Braunschweig, 1925.

21a. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. **XI**, p. 650.

21b. Boer, Broos, Emmens, *Z. anorg. Chem.*, **191**, 120 (1931).

Purification of Tungstic Acid:

22. *Edelerden und Erze*, **3**, 49, 65 (1922).

23. Smithells, C. J., *Ibid.*, p. 19–21.

23a. Smith and Exner, *Chem. News*, **90**, 37, 49 and 66 (1904).

24. Gin, Gustave, *Ibid.*, 502.

25. Gin, Gustave, *Ibid.*, 506.

Production of Tungsten Powder:

26. Smithells, C. J., *Ibid.*, pp. 29–30.

27. Spitzin, V., *Zeit. anorg. Chem.*, **148**, 69 (1925); *Zeit. anal. Chem.*, **75**, 440 (1928).

28. Liempt, J. A. M. van, *Zeit. anorg. Chem.*, **181**, 425 (1929).

29. Davis, C. W., "The Reduction of Tungstic Oxide", *J. Ind. Eng. Chem.*, **11**, 201–4 (March, 1919).

30. Ullmann, "Enzyklopädie des Technischen Chemie", **10**, p. 517 (1932).

31. *Zeit. anorg. Chem.*, **65**, 314 (1909).

32. Kahlenberg, L., and Kahlenberg, H. H., "The Preparation of Metallic Tungsten and some of its Alloys", *Trans. Am. Electrochem. Soc.*, **46**, 189–190 (1924).

33. Gin, Gustave, *Ibid.*, 516–6.

34. *Pogg. Ann.*, **136**, 16, 241 (1867).

35. Gin, Gustave, *Ibid.*, 517.

36. *Zeit. anorg. Chem.*, **65**, 321 (1910).

37. *J. Chem. Soc.*, 2394 (1929).

37a. Ma, C. C., "Pure Tungsten Direct from Ore", Doctorate Dissertation, Columbia University, N. Y. (1943).

37b. Fink, C. G., and Ma, C. C., "Pure Tungsten Direct from Ore", *Trans. Electrochem. Soc.*, **84**, 33–63 (1943).

38. *Quarterly Review Am. Electropl. Soc.*, **19**, 41 (1933).

39. *Zeit. Electrochem.*, **30**, 474 (1924).

39a. Holt, N. L., and Nielsen, M. L., "Electrodeposition of Nickel-tungsten Alloys from an Acid Plating Bath", The Electrochemical Society, Reprint 82-3 (Oct. 12, 1942).

39b. Holt, M. I., and Black, Rodney, E., "Electrodeposition of Iron-tungsten alloys from an Acid Plating Bath", The Electrochemical Society, Reprint 82-27 (Oct. 12, 1942).

40. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", **XI**, p. 838 (1931).

41. *Zeit. Elektroch.*, **31**, 249 (1925).

42. *Rec. Trav. Chim.*, **50**, 1050 (1931).

43. *Trans. Am. Electrochem. Soc.*, **46**, 185 (1924).

44. *Compt. rend.*, **184**, 91 (1927).

45. *Zeit. anorg. Chem.*, **65**, 302 (1910).

46. Hartmann, Ebert and Bretschneider, *Zeit. anorg. Chem.*, **198**, 116 (1931).

47. Leo, Shoo-Tze, and Shen, Tsing-Nang, "Electrolytic Production of Tungsten Metal from a fused Phosphate Bath", *Electrochem. Soc.*, **66**, 461 (1934).

48. *Zeit. Electrochem.*, **31**, 249 (1925).

49. Smithells, Colin J., *Ibid.*, p. 46–47.

Manufactured of Ductile Tungsten:

50. Sykes, W. P., "Powder Metallurgy", *Metal Progress*, 27 (March, 1934).

51. Smithells, C. J., *Ibid.*, p. 23.

52. Cregg, J. L., "The Alloys of Iron and Tungsten", p. 15, New York (McGraw-Hill Book Co.), 1934.

53. Smithells, C. J., *Ibid.*, p. 54.

54. Wulff, John, "Powder Metallurgy", p. 433, Cleveland, American Society for Metals, 1942.

54a. Baëza, Walter J., "A Course in Powder Metallurgy", New York, Reinhold Publishing Corp., 1943.

Tungsten Carbides:

55. Becker, K., "Hochschmelzende Hartstoffe", Berlin, Verlag Chemie, 1933.

56. Bird, T. R., "Tungsten", by C. J. Smithells, Chapter XIII, 1936.

57. Gmelin's "Handbuch der anorganischen Chemie", pp. 192–199.

58. Jones, W. D., "Principles of Powder Metallurgy", Chapter V., pp. 157–170, London, Edward Arnold & Co., 1939.

59. Fink, C. G., "Tungsten Carbides", *Foote-Prints*, VI, No. 2, 1–15, (Dec., 1933).
60. Hoyt, S. L., "Hard Metal Carbides and Cemented Tungsten Carbide", *Trans. Am. Inst. Min. Met. Eng., Inst. Met. Div.*, **89**, 9–58 (1930).
61. McKenna, P. M., "Hard Intermetallic Compounds for New Metal Cutting Tools", *Metal Progress*, 152–155 (Aug., 1929).
62. Wulff, John, "Powder Metallurgy", p. 468, Cleveland, American Society for Metals, 1942.

Ferro-tungsten:

63. Rossi, A. J., "Ferro-alloys", *Mineral Industry*, **11**, 693–6 (1902).
64. Gin, Gustav, *Ibid.*, p. 517.
65. Yelyutin, V., "Complex-Thermal Production of Ferrotungsten", *Novosti Tekeniki*, **7**, 27–28 (1938).
66. Keeney, R. M., *Am. Inst. of Min. & Met. Eng.*, Bull. **140**, 1337–1341 (Aug., 1918).
67. Dailey, J. G., "Acid Electric Furnace Ferrotungsten", *Am Institute of Chem. Eng.* (Dec. 5, 1919); Raw Material II, No. 2, 67–71 (Feb., 1920).
68. *J. Ind. Eng. Chem.*, **4**, 388 (1912).

Chapter V

The Chemistry of Tungsten

1. THE PHYSICAL PROPERTIES OF TUNGSTEN

Atom

Isotopes: 182, 183, 184, 186 (percentage abundance, 22.6, 17.2, 30.1, 30.0 per cent respectively)

Atomic Number: 74.

Type of Lattice: Body-centered Cubic, $a = 3.159$ Å.

Atomic weight: 183.92 (International Committee for 1939).

Atomic Volume: 9.59 (based on atomic weight 184 and specific gravity 19.2)

Crystallization

Cubic

Color

Steel-grey, with a strong metallic luster (using carbon reduction process, J. J. Y. F. Elhuyar); black and fine-grained (if reduced slowly at low temperature, F. Wöhler, J. J. Berzelius, H. E. Roscoe, and M. E. Pennington); silver-grey or tin-white (by hydrogen reduction, F. Wöhler).

Specific Gravity

19.0 to 19.3	(H. Alterthum)	
19.35	(W. Geiss and J. A. M. van Liempt)	
19.37	(H. C. Burger)	
19.295	(E. A. Owen)	
18.81	before drawing into wire	
19.30	after drawing into wire 150 mils dia.	(C. G. Fink)
19.58	“ “ “ “ 10 “ “	
19.86	“ “ “ “ 1.5 “ “	

Hardness

6.5 to 7.5 (L. Weiss)

Tensile Strength

According to Z. Jeffries:

		lbs sq in
Ingot	200 × 250 mils	18,000
Swaged rod	216 mils dia.	50,000
" "	125 " "	107,000
" "	80 " "	176,600
" "	26 " "	215,000
Drawn wire	18 " "	264,000
" "	7.23 " "	340,000
" "	5.78 " "	366,000
" "	5.50 " "	378,000
" "	3.96 " "	483,000
" "	1.4 " "	590,000

Elastic Limit

$E = 3.886 \times 10^{12}$ dynes per sq. cm. (S. J. Wright)
$= 41.4 \times 10^{11}$ " " " " (C. G. Fink)
$= 38.7 \times 10^{11}$ " " " " (for swaged tungsten) (A. L. Kimball and D. E. Lovell)

Compressibility

At 20° is 0.28×10^{-6} per megabar, the smallest of any known metal (L. Weiss)

Coefficient of Thermal Expansion

$a = 0.0_538$ between 1000° and 1500° (I. Langmuir)
$a = 0.0_544$ between 1500° and 2000° (I. Langmuir)

Modulus of Elasticity (single crystal)

about 36,000 kg/mm^2

Modulus of Torsion (single crystal)

15,000–22,000 kg/mm^2

Thermal Conductivity

0.35 cal per cm per degree (W. D. Coolidge)
0.38_3 " " " " " (S. Weber)

Specific Heat

0.03342 (H. V. Regnault)
0.0358 (L. Weiss)

0.0336 between 0° and 100° (H. Mache)
0.033 at 340°; 0.036 at 1000°; 0.041 at 1350° (M. von Pirani)

Melting Point

2800° to 2850° (H. von Wartenberg); 3080° (C. W. Waidner and G. K. Burgess); 3267° (I. Langmuir); 3410° ± 20° (U. S. Bureau of Standards)

Boiling Point (760 mm Hg)

about 5900°

Mean Coefficient of Thermal Expansion

4.6×10^{-6} at 0–500°

Heat of Fusion

about 60 cal/g

Heat of Vaporization at Normal Boiling Point

about 1150 cal/g

Vapor Pressure of Metal

3×10^{-5} mm Hg at 2600°

Vapor Pressure of Metallic Oxide

760 mm Hg at 1400°

Electrical Conductivity

20.0×10^4 ohms at 0° (I. Langmuir)
18.9×10^4 " " " (H. Pécheux)

Resistivity (Special Resistance)

5.5 microhms/cm^3 at 20°
25.5 microhms/cm^3 at 750° Specific Resistance

Temperature Coefficient of Resistivity

4.8×10^{-3}

Work Function

4.5 volts

Ionization Voltage

8.1 volts

Thermionic Emission

1 ma/cm² at 1950°K

Total Radiation

about 0.3 watts/cm² at 800°K
about 4.0 watts/cm² at 1400°K
about 25.0 watts/cm² at 2000°K
about 84.0 watts/cm² at 2600°K

Radiation for 5500Å (in per cent of the radiation of the black body)

48 per cent at 20°

Reflectivity for 5500Å

50 per cent at 20°

Wave Length of the Characteristic X-ray Radiation

about 0.21Å K-Series
about 1.48Å L-Series

Velocity of Sound

about 4,300 m/sec
about 13,000 ft/sec

2. THE CHEMICAL PROPERTIES OF TUNGSTEN

Hydrogen, according to A. Sieverts and E. Bergner, is very little absorbed by tungsten below 1200°. Tungsten hydride, presumably WH_3, was obtained by T. Weichselfelder and B. Thiede. Hydrogen sulfide gives superficial reaction at red heat.

J. Férée found that the finely divided metal is pyrophoric in air; and according to E. Zettnow and L. von Uslar, tungsten trioxide is formed when the finely divided metal is heated in air.

According to I. Langmuir, tungsten wire, when heated in oxygen at about 800° K under low pressure, oxidizes to WO_3, which will volatilize upon further heating to 1200° K, leaving the metal clean and bright.

J. J. and F. de Elhuyar and A. Riche observed that at red heat tungsten is oxidized by water vapor to form a mixture of the trioxide and the blue oxide.

Fluorine attacks tungsten at ordinary temperature, forming a volatile fluoride (H. Moissan). Dry chlorine, free from air, attacks tungsten at 250–300°, forming the hexachloride, but if air or moisture is present, two oxychlorides are formed (A. Riche, H. Davy, and L. Weiss). Bromine attacks tungsten at a bright red-heat, forming the pentabromide

(J. B. von Borck); if atmospheric moisture is present, an oxybromide is formed (A. Riche). A diiodide is formed when tungsten at red heat is attacked by iodine (A. E. Roscoe).

Hydrofluoric and hydrochloric acids have very little effect on tungsten, if any. According to Ruder only hydrochloric acid acts on wrought tungsten at 110° after 175 hours when a thin adherent coating of tungsten oxide is formed, which protects the metal against further action.

Molten or boiling sulfur acts slowly on tungsten (A. Riche and J. B. von Borck). Heated tungsten is attacked by the vapor of carbon disulfide, forming tungsten disulfide (A. Riche). Hydrogen sulfide darkens the surface of tungsten at red heat (L. Weiss). With sulfur dioxide, a little blue, green or brown oxide is formed (C. H. Ehrenfeld).

Sulfuric acid acts on tungsten, forming a blue liquid (A. Riche), as well as sulfur dioxide and some intermediate tungsten oxides with concentrated acid at a high temperature (E. D. Desi).

Sulfur, either molten or boiling, gives slow reaction on tungsten.

Nitrogen, up to 1500° does not attack tungsten (H. Moissan). The dinitride is formed when nitrogen is present in an incandescent tungsten filament at 2300° (C. J. Smithells and H. P. Rooksby). Warm nitric acid easily oxidizes tungsten to the yellow trioxide (L. von Uslar, E. Zettnow, A. Riche, and H. Moissan). A mixture of nitric and hydrofluoric acid acts on tungsten with the formation of tungsten trioxide (W. E. Ruder and H. Moissan). Aqua Regia causes superficial oxidation to WO_3 at room temperature.

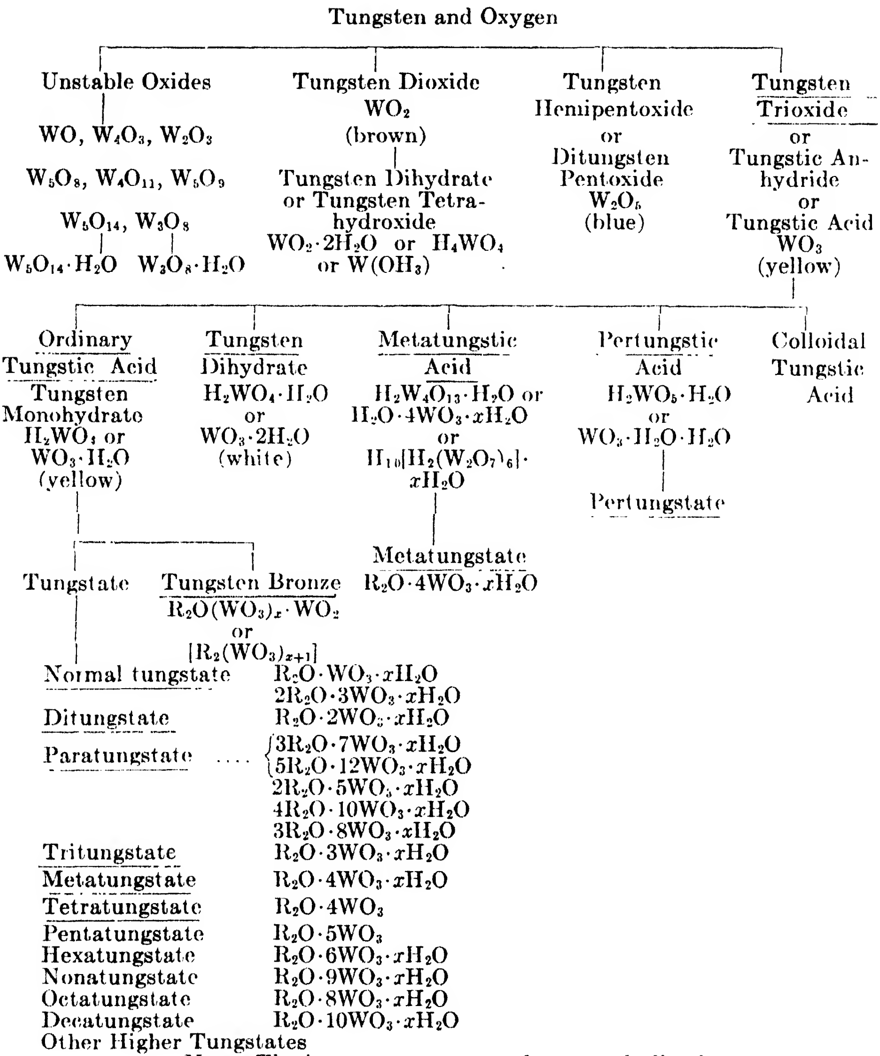
Aqueous ammonia has no effect on tungsten. Carbon dioxide causes the formation of oxide at 1200° while carbon monoxide gives rise to the formation of W_2C_4 at 1000°. Ammonium hydroxide and aqueous potassium hydroxide or sodium hydroxide have practically no effect on tungsten, while the latter in molten condition slowly oxidizes it in air. Tungsten is soluble in basic solution of $K_3Fe(CN)_6$ in saturated solution of $NaClO_3$ and in sodium nitrite at 300°.

According to Ruder, tungsten dissolves slowly in fused sodium carbonate, potassium carbonate or mixtures of the two. The addition of potassium nitrate hastens the reaction.

Tungsten and Oxygen

Of all the compounds of tungsten, those of tungsten and oxygen are the most important and interesting. A satisfactory classification of these compounds is a difficult matter. But for the purpose of presentation and discussion of these compounds the accompanying diagram, showing their general relationship, is given.

About a dozen tungsten oxides have been described; but all except



Tungsten and Oxygen

Unstable Oxides
WO, W_4O_3, W_2O_3
W_5O_8, W_4O_{11}, W_5O_9
W_5O_{14}, W_3O_8
$W_5O_{14} \cdot H_2O$ $W_3O_8 \cdot H_2O$

Tungsten Dioxide
WO_2
(brown)
Tungsten Dihydrate or Tungsten Tetrahydroxide
$WO_2 \cdot 2H_2O$ or H_4WO_4 or $W(OH_3)$

Tungsten Hemipentoxide or Ditungsten Pentoxide
W_2O_5
(blue)

Tungsten Trioxide or Tungstic Anhydride or Tungstic Acid
WO_3
(yellow)

Ordinary Tungstic Acid
Tungsten Monohydrate
H_2WO_4 or $WO_3 \cdot H_2O$
(yellow)

Tungsten Dihydrate
$H_2WO_4 \cdot H_2O$ or $WO_3 \cdot 2H_2O$
(white)

Metatungstic Acid
$H_2W_4O_{13} \cdot H_2O$ or $H_2O \cdot 4WO_3 \cdot xH_2O$ or $H_{10}[H_2(W_2O_7)_6] \cdot xH_2O$

Pertungstic Acid
$H_2WO_5 \cdot H_2O$ or $WO_3 \cdot H_2O \cdot H_2O$

Colloidal Tungstic Acid

Pertungstate

Metatungstate
$R_2O \cdot 4WO_3 \cdot xH_2O$

Tungstate

Tungsten Bronze
$R_2O(WO_3)_x \cdot WO_2$ or $[R_2(WO_3)_{x+1}]$

Normal tungstate	$R_2O \cdot WO_3 \cdot xH_2O$ $2R_2O \cdot 3WO_3 \cdot xH_2O$
Ditungstate	$R_2O \cdot 2WO_3 \cdot xH_2O$
Paratungstate	$\begin{cases} 3R_2O \cdot 7WO_3 \cdot xH_2O \\ 5R_2O \cdot 12WO_3 \cdot xH_2O \end{cases}$ $2R_2O \cdot 5WO_3 \cdot xH_2O$ $4R_2O \cdot 10WO_3 \cdot xH_2O$ $3R_2O \cdot 8WO_3 \cdot xH_2O$
Tritungstate	$R_2O \cdot 3WO_3 \cdot xH_2O$
Metatungstate	$R_2O \cdot 4WO_3 \cdot xH_2O$
Tetratungstate	$R_2O \cdot 4WO_3$
Pentatungstate	$R_2O \cdot 5WO_3$
Hexatungstate	$R_2O \cdot 6WO_3 \cdot xH_2O$
Nonatungstate	$R_2O \cdot 9WO_3 \cdot xH_2O$
Octatungstate	$R_2O \cdot 8WO_3 \cdot xH_2O$
Decatungstate	$R_2O \cdot 10WO_3 \cdot xH_2O$
Other Higher Tungstates	

Note: The important compounds are underlined

three of them are unstable, and their individuality and identity have not been well established.

The series of unstable oxides consists of: WO, W_4O_3, W_2O_3, W_5O_{14}, W_5O_8, W_4O_{11}, W_5O_9, W_3O_8. The other three well-defined oxides of tungsten are: tungsten dioxide, WO_2 (brown), tungsten hemipentoxide, W_2O_5 (blue), and tungsten trioxide, WO_3 (yellow).

Some of the unstable oxides appear to be identical with, or mixtures containing, tungsten hemipentoxide.

WO is the labile intermediate product appearing as an adsorption layer on metallic tungsten when it is acted upon by oxygen. E. D. Desi regarded W_2O_3 and W_5O_9 as combination of $WO \cdot WO_2$ and $WO_3 \cdot 2WO_2 \cdot 2WO$, respectively. Another series of blue-colored oxides, supposed to be intermediate between the di- and trioxides, has been reported. The hydrates of W_5O_{14} and W_3O_8 are known: tungsten pentitatetradecoxide, $W_5O_{14} \cdot H_2O$, and tungsten tritaoctoxide, $W_3O_8 \cdot H_2O$. The former forms a dark blue powder with a purplish luster, and the latter a brown mass resulting from the action of aqueous ammonia on the pentitatetradecoxide.

Tungsten dioxide, WO_2, may be obtained as an intermediate product in the reduction of tungsten trioxide by hydrogen. According to the Westinghouse Metal Filament Co., the dioxide is formed when a mixture of the trioxide, free from alkali, and one-tenth to one-fifth its weight of glycerol or ethylene glycol, is heated with carbon in a covered crucible at a dull red heat. It may also be formed by heating tungsten di-iodide to 500° in a current of carbon dioxide.

The dioxide is brown in color. Its specific gravity, according to C. J. B. Karsten, is 12.1; it smelts under cover of nitrogen between 1500 and 1600° and begins to sublime at 800°. It dissociates between 1500 and 1600° into W and WO_3. Hydrogen reduces it at high temperature to the metal and carbon at about 1020°.

R. F. Bernhardi-Grisson obtained the dihydrate, $WO_2 \cdot 2H_2O$ from the electrolytic reduction of solution of the dioxide in hydrofluoric or hydrochloric acid.

Tungsten hemipentoxide, W_2O_5 (ditungsten pentoxide), is intermediate between the dioxide and the trioxide, and may be formed by oxidation of the former or by reduction of the latter. Malaguti prepared it by heating the trioxide at 250 to 300° in a current of hydrogen. The hemipentoxide may also be obtained by carefully heating ammonium paratungstate in a closed crucible, by boiling a solution of a tungstate in hydrochloric acid, or by decomposition of tungsten pentachloride or pentabromide by means of water. The color of W_2O_5 varies from greenish blue to deep blue. It begins to sublime at 800°. On heating, it sinters to WO_2 and WO_3. At red heat in a current of HCl, the reaction $3W_2O_5 + 10HCl = W + 5WO_2Cl_2 + 5H_2O$ occurs.

Tungsten trioxide, WO_3 (tungstic anhydride or "tungstic acid") is the most important of the compounds of tungsten and oxygen. It occurs in nature as tungstite and is the principal component of wolframite, ferberite, hübnerite and scheelite.

The extraction of the trioxide from the ores, just mentioned, has been treated in the chapter on metallurgy.

Pure tungsten trioxide is a bright canary-yellow, amorphous powder, which changes to orange when heated, but regains its original color on cooling. Crystals of the trioxide, as obtained by A. E. Nordenskjöld, were small, bright-yellow rhombic prisms, while those obtained by H. Debray were octahedral; some were yellow and translucent, others dark green and opaque.

Specific gravity:

6.13 for the amorphous, yellow oxide (J. J. and F. de Elhuyar)
5.274 at 16.5° (W. Herapath)
6.302 to 6.384 (A. E. Nordenskjöld)
7.1306 (C. J. B. Karsten)

$$\left.\begin{array}{l}7.16 \text{ at } 17^\circ \text{ for the amorphous oxide}\\ 7.232 \text{ at } 17^\circ \text{ for the crystals}\end{array}\right\}\text{(E. Zettnow)}$$

Specific heat:

0.0798 (H. V. Regnault)
0.0894 (H. Kopp)
0.0442 between −189° and −80.9° (A. S. Russell)
0.0678 " −75.8° " 0° " " "
0.0783 " 2.3° " 46.6° " " "

Melting point:

1473° (F. M. Jäger and H. C. Germs).

Sinter temperature:

about 900° giving a little W_2O_5.

Crystallization:

rhombic prisms (A. E. Nordenskjöld)
octahedral (H. Debray)

Heat of formation:

(a) for $W + 1\frac{1}{2}O_2 = WO_3$
+196.44 Cals at constant volume } M. Delépine
+197.3 Cals at constant pressure } L. A. Hallopean
+192.6 Cals (L. Weiss and A. Stimmelmayer)
+194.9 Cals (J. E. Moose and S. W. Parr)
+195 ± 1 Cals (J. A. M. Van Liempt)
+199.9 Cals (Z. Shibata)
(b) for $WO_2 + \frac{1}{2}O_2 = WO_3$
+61.8 Cals (Z. Shibata)
+64.9 Cals (M. Delépine and L. A. Hallopean)
(c) for $\frac{1}{2}W_2O_5 + \frac{1}{4}O_2 = WO_3$
+30.3 Cals (Z. Shibata)

Tungsten trioxide, when heated with carbon, yields the blue oxide between 650 and 850°, a dark-brown mixture of oxides between 900 and 1050°, and metallic tungsten above 1050°. When hydrogen is used as the reducer, the trioxide yields the mixture of brown oxides between 800 and 900° and a deposit of the metal at 1080°. When aluminum or zinc is heated with the oxide, the metal is formed.

Tungsten trioxide is insoluble in water; and the only acid that dissolves it is hydrofluoric acid. It is soluble in solutions of alkali hydroxides and carbonates, yielding tungstates.

Tungsten trioxide, WO_3, is reduced to the dioxide, WO_2, if hydrogen is passed through water at 85° C and the mixture of hydrogen and water vapor is then passed over the trioxide at 900° C; however, the pentoxide, W_2O_5, results when the temperature of the water is maintained at 97° C.

When the trioxide is heated with chlorine, the yellow oxychloride, WO_2Cl_2, is formed. But bromine and iodine do react on it. Gaseous ammonia reacts to form the oxy-amidonitride. According to C. Matignon, a carbide is formed when carbon is heated at 2000° with the trioxide.

The Hydrates of Tungsten Trioxide. Four well-defined hydrates of tungsten trioxide are known:

(a) Tungsten Monohydrate (ordinary tungsten acid): H_2WO_4 or $WO_3 \cdot H_2O$ (yellow)

(b) Tungsten Dihydrate: $H_2WO_4 \cdot H_2O$ or $WO_3 \cdot 2H_2O$ (white)

(c) Metatungstic Acid: $H_2W_4O_{13} \cdot xH_2O$ or $H_2O \cdot 4WO_3 \cdot xH_2O$

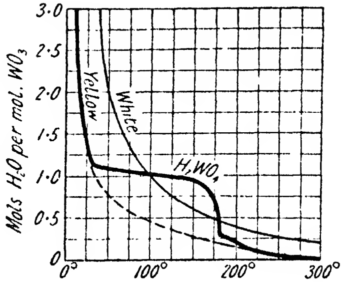
(d) Pertungstic Acid: $WO_3 \cdot H_2O_2 \cdot H_2O$

Several other hydrates have been described but their existence is doubtful. They are: $2WO_3 \cdot H_2O$, $3WO_3 \cdot H_2O$, $4WO_3 \cdot H_2O$, $5WO_3 \cdot 3H_2O$, $8WO_3 \cdot 3H_2O$.

With bases, the monohydrate and the dihydrate produce the same series of salts.

Tungsten Monohydrate and Dihydrate. The preparation of tungstic acid, H_2WO_4, has been discussed in the chapter on metallurgy. Tungstic acid is an amorphous yellow substance. The white dihydrate, $H_2WO_4 \cdot H_2O$, is formed when cold hydrochloric acid is added to a solution of an alkali tungstate. N. Nakazama and T. Okada prepared tungstic acid by evaporating a solution of the trioxide in concentrated hydrochloric acid and by passing steam into the solution of the trioxide in concentrated hydrochloric acid. Both hydrates are insoluble in water, but may form colloidal solution.

The results of observations on both yellow and white preparations are given in the accompanied temperature-composition curves. "The yellow oxide forms one and only one hydrate $WO_3 \cdot H_2O$, and the white voluminous compound is a hydrous oxide, the water content varying continuously with change in temperature. The curve for the yellow oxide is reproducible; but the ease with which the white compound gives up its water is determined by the size of the hydrous particles. Thus, the curve for the very highly dispersed β oxide lies above that for the coarser α oxide throughout the entire range of the investigation. The crystal structure of the white hydrous oxide is apparently different from that of the yellow monohydrate or yellow WO_3. If this be true, it means that the oxide exists in two forms and not that the white compound is a hydrate, as Burger supposed. The white oxide becomes yellow on standing; and the yellow oxide sometimes takes on a greenish color which has been traced to the presence of a lower oxide, possibly W_2O_5"*



Dehydration curves of the white and yellow hydrates of tungsten trioxide. *After J. W. Mellor.*

Metatungstic Acid. The individuality of metatungstic acid has definitely been proved, although, by itself, it easily disintegrates. The following formulas have been given in the literature:

$H_2W_4O_{13}\cdot 8H_2O$ (C. Scheibler and F. Kohn)
$H_2W_4O_{13}\cdot 8.5H_2O$ (H. Copaux)
$H_2W_4O_{13}\cdot 9H_2O$ (M. Sobolew)
$H_{10}[H_2(W_2O_7)_6]$ (H. Copaux)
$H_{10}[H_2(W_2O_7)_6]\cdot 22H_2O$ (A. Rosenheim and J. Jaenicke)

Metatungstic acid is obtained by decomposing lead metatungstate with hydrogen sulfide thus: $PbW_4O_{13} + H_2S = H_2W_4O_{13} + PbS$. It may be prepared by treating a solution of ammonium salt with hydrochloroplatinic acid, filtering off ammonium chloroplatinate, and evaporating the filtrate for crystallization.

Metatungstic acid is soluble in water, its solubility depending upon temperature.

The crystals of metatungstic acid are octahedra, according to V. Forcher and tetragonal bipyramids, according to C. Sheibler. They effloresce

---

* Weiser, H. B. "The Hydrous Oxides", p. 289, McGraw-Hill Book Co., 1926.

readily in the air and have a density of 3.93. On heating, the crystals lose water, becoming anhydrous at about 180°.

Pertungstic Acid. By treating tungsten trioxide with a two per cent solution of hydrogen dioxide at boiling point, J. B. Cammerer obtained a deep orange, amorphous substance of pertungstic acid, $H_2WO_5 \cdot H_2O$ or $WO_3 \cdot H_2O_2 \cdot H_2O$. It dissolves with great difficulty in cold water.

An amorphous substance, perditungstic acid, $H_2W_2O_8 \cdot 2H_2O$ or $W_2O_7 \cdot 3H_2O$, is known. It decomposes at about 35°.

Colloidal Tungstic Acid. When dilute hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes slightly acid, a colloidal solution of tungstic acid is formed. However, if the solution is heated to boiling and is run into boiling hydrochloric acid solution, tungstic acid is precipitated.

N. Pappada recommended preparing the colloid by the following procedure:

"Hydrochloric acid is added to a concentrated solution of sodium tungstate until the liquid has an acidic reaction. The white, gelatinous precipitate is washed several times by decantation at a low temp., 0° to 5°, while protecting the precipitate from currents of air which produce a change in the colloid. Fifteen parts of the tungstic acid are then dissolved by gently warming with a concentrated solution of one part of oxalic acid and the liquid dialyzed. If the outer water is frequently changed, the oxalic acid is completely removed, leaving a colloidal solution of tungstic acid which may be concentrated *in vacuo* over sulfuric acid at ordinary temperature until it contains as much as 1.25 per cent WO_3."

According to A. V. Dumansky and A. P. Buntin, the reaction of hydrochlorid acid in sodium tungstate solution takes place in stages: $Na_2WO_4 + 2HCl = H_2WO_4 + 2NaCl$ and $H_2WO_4 + Na_2WO_4 = Na_2O \cdot 2WO_3 + H_2O$, which is repeated until a colloidal particle of the composition $Na_2O \cdot nWO_3$ or $H_2(WO_4 \cdot nWO_3)$ is obtained.

With various organic reducing agents, such as formaldehyde, sucrose, glucose, dextrin, etc., colloidal solutions of tungstic acid yield intensely blue solutions on exposure to light. However, if the solution is kept for some time, the blue coloration is not shown when the solution is exposed to light; but if the solution is heated, the blue reduction products are obtained. It is, therefore, assumed that colloidal tungstic acid exists in two modifications, one being photochemically sensitive and the other not.

Tungstates

Tungstates, arranged in the following list, have been known and described. But only a few of them are recognized as a well-defined series of salts, while the individuality of the others has not been fully established.

(1) Monotungstate (Normal Tungstate)	$R_2O\cdot WO_3\cdot xH_2O$
	$2R_2O\cdot 3WO_3\cdot xH_2O$
Ditungstate	$R_2O\cdot 2WO_3\cdot xH_2O$
Paratungstate	$\left\{\begin{array}{l}3R_2O\cdot 7WO_3\cdot xH_2O\\ 5R_2O\cdot 12WO_3\cdot xH_2O\end{array}\right.$
	$2R_2O\cdot 5WO_3\cdot xH_2O$
	$4R_2O\cdot 10WO_3\cdot xH_2O$
	$3R_2O\cdot 8WO_3\cdot xH_2O$
Tritungstate	$R_2O\cdot 3WO_3\cdot xH_2O$
Metatungstate	$R_2O\cdot 4WO_3\cdot xH_2O$
Tetratungstate	$R_2O\cdot 4WO_3$
Pentatungstate	$R_2O\cdot 5WO_3$
Hexatungstate	$R_2O\cdot 6WO_3\cdot xH_2O$
Octotungstate	$R_2O\cdot 8WO_3\cdot xH_2O$
Decatungstate	$4R_2O\cdot 10WO_3\cdot xH_2O$
and other higher tungstates	
(2) Pertungstate	
(3) Tungsten Bronze	$R_2O(WO_3)_x\cdot WO_2$

Of the above, only the normal tungstates paratungstates, metatungstates, tungsten bronzes and pertungstates have been accurately investigated and their existence established beyond doubt. The di- and tritungstates and a few of the higher tungstates have been described, but their nature in some cases has not been determined.

The Monotungstates (Normal Tungstates). The normal tungstates of the alkalies can be produced by fusing together tungsten trioxide and the alkali hydroxide or carbonate in equivalent proportions. Tungstates of the heavier metals are produced by fusing together an alkali tungstate and the chloride of the metal. The tungstates of the alkali metals and of magnesium are soluble in water, while those of other metals are only slightly soluble in water and in dilute acids. They can be decomposed by concentrated mineral acids (phosphoric acid excepted) with separation of tungstic acid. Paratungstates behave similarly to the acids, whereas metatungstates do not.

Zinc chloride reacts on a solution of tungstate, giving a yellow precipitate, which turns blue upon heating with dilute hydrochloric or sulfuric acid. A mixture of a solution of alkali tungstate with hydrochloric acid in excess, gives rise to brilliant colors, from red to blue, when it is reduced by zinc.

Aluminum Tungstate. The normal salt, $Al_2(WO_4)_3\cdot 8H_2O$ or $Al_2O_3\cdot 3WO_3\cdot 8H_2O$, is obtained when solutions of alum and the monotungstate are mixed.

Ammonium Tungstates. It has been found that normal ammonium tungstate, $(NH_4)_2WO_4 \cdot xH_2O$, cannot be isolated, since ammonia is lost on concentration and an acid salt remains. It may be obtained as a white mass by the addition of hydrated tungstic acid to liquid ammonia.

Antimony Tungstate. The normal salt appears to be formed when solutions of normal sodium tungstate and tartar-emetic are mixed. However, the white precipitate is decomposed by washing with water. The higher tungstates of antimony will be discussed under the section on the higher tungstates.

Barium Tungstate. G. Tammann observed that when a mixture of barium and tungsten oxides is heated between 300 and 550°, barium tungstate, $BaO \cdot WO_3$, results. It may be obtained by fusing together sodium tungstate, sodium chloride and barium chloride. It crystallizes in colorless octahedra. It is slightly soluble in water and fuses with difficulty, becoming incandescent at red heat.

Beryllium Tungstates. Complex salts, corresponding to the formulae $xBeCl_2 \cdot yBeWO_4 \cdot zBeO$ and $xBe(NO_3)_2 \cdot yBeWO_4 \cdot zBeO$, have been prepared.

Bismuth Tungstate. Normal bismuth tungstate is obtained when an intimate mixture of bismuth and tungsten trioxides in the theoretical proportions is fused and is allowed to cool slowly.

Cadmium Tungstates. The anhydrous normal salt, $CdWO_4$ or $CdO \cdot WO_3$, is obtained when a mixture of sodium tungstate, cadmium chloride and sodium chloride is melted together and the product leached with boiling water. The dihydrate, $CdWO_4 \cdot 2H_2O$, is obtained as a white powder, by treating a solution of a cadmium salt with sodium or potassium tungstate.

Calcium Tungstate. The normal tungstate, $CaWO_4$, occurs in nature as scheelite. It may be prepared by fusing together sodium tungstate and anhydrous calcium chloride, either with or without the addition of sodium chloride; the crystals thus obtained are similar in form to scheelite, that is, tetragonal bipyramids. The amorphous form is obtained by mixing solution of normal potassium or sodium tungstate with a feebly acidified solution of calcium chloride.

Cerium Tungstate, $Ce_2(WO_4)_3$, is obtained by igniting the pale-yellow precipitate formed from a mixture of cerium sulfate and sodium tungstate.

Cobalt Tungstate, $CoWO_4$, is obtained by fusing together sodium tungstate, sodium chloride and cobalt chloride. The crystals thus obtained are greenish-black in color. The hydrate, $CoWO_4 \cdot 2H_2O$, is obtained as a violet precipitate when a solution of alkali tungstate is treated with a cobalt salt.

Copper Tungstates, $CuWO_4$. In nature copper tungstate occurs as cupro-tungstite and cupro-scheelite. According to G. Tammann, copper tungstate is formed when a mixture of equimolecular proportions of cupric oxide and tungsten trioxide is heated between 600 and 800°. The hydrate form, $CuWO_4 \cdot 2H_2O$, is obtained by the addition of a cupric salt to a normal tungstate solution. The precipitate, thus obtained, is light green in color, which becomes brownish on heating, with loss of water. It is insoluble in water, but soluble in ammonia, phosphoric acid, or acetic acid.

The following salts are known:

Cuprous Cupric tungstate, $Cu_2WO_4 \cdot 2CuWO_4$
Copper Diammino-tungstate, $CuWO_4 \cdot 2NH_3 \cdot H_2O$
Copper Tetrammino-tungstate, $CuWO_4 \cdot 4NH_3$

Iron Tungstates. The series of iron tungstate salts, occurring as the minerals ferberite, hübnerite and wolframite, has already been described.

The ferrous tungstate, $FeWO_4$, may be obtained by fusing a mixture of ferrous oxide with tungsten trioxide between 480 and 700°. When a mixture of sodium tungstate, ferrous chloride, and sodium chloride (1:2:2) is fused, crystals of artificial ferberite are formed. The trihydrate, $FeWO_4 \cdot 3H_2O$, is obtained as a light-brown powder by adding a solution of a ferrous salt to one of sodium tungstate. The trihydrate is not soluble in water and is not dissolved by cold hydrochloric, sulfuric, or nitric acid. It is, however, dissolved by the boiling acids, with the separation of tungsten trioxide.

Lanthanum Tungstate. According to F. R. M. Hitchcock, by adding a solution of sodium tungstate to one of lanthanum chloride, in the presence of alcohol, a white precipitate is obtained, presumably lanthanum tungstate, which has a delicate blue color on drying.

Lead Tungstate. The normal salt occurs native as the minerals stolzite and raspite. It may be obtained as a white flocculent precipitate slightly soluble in water by adding a solution of lead salt to one of alkali tungstate. When sodium tungstate and lead chloride or lead sulfate are fused together, crystals of lead tungstate are formed. The crystals are octahedral and colorless, insoluble in water and nitric acid, but soluble in alkalies.

Lithium Tungstate, Li_2WO_4. This normal salt is obtained by dissolving tungsten trioxide in a boiling solution of lithium carbonate, and evaporating the solution for crystallization. The octahedral crystals readily dissolve in water, yielding an alkaline solution. The hydrate, $Li_2WO_4 \cdot H_2O$, is known.

Magnesium Tungstate, $MgWO_4$. The anhydrous salt is formed by fusing a mixture of sodium tungstate, magnesium chloride and sodium chloride. The trihydrate, $MgWO_4 \cdot 3H_2O$, is formed by mixing solutions of sodium tungstate and magnesium acetate in equal proportions in the presence of alcohol. The heptahydrate, $MgWO_4 \cdot 7H_2O$, is obtained by boiling tungstic acid and magnesium carbonate suspended in water. The precipitate thus formed readily dissolves in hot water on cooling. Potassium magnesium tungstate, presumably of the formula $K_2WO_4 \cdot MgWO_4 \cdot 2H_2O$, is formed if a concentrated aqueous solution of the heptahydrate is mixed with one of potassium tungstate.

Manganese Tungstate, $MnWO_4$. The anhydrous normal salt, $MnWO_4$, occurs in hübnerite and as a component in wolframite. By treating a solution of a manganous salt with normal sodium tungstate, a greyish-white powder of manganous tungstate dihydrate, $MnWO_4 \cdot 2H_2O$, is obtained. It is insoluble in cold hydrochloric acid, but is soluble in warm phosphoric or oxalic acid. When the dihydrate is ignited, it loses water and becomes pale yellow. The pale-brown anhydrous salt, $MnWO_4$, may be obtained by melting a mixture of sodium tungstate, manganous chloride and sodium chloride (1:2:2) in a covered crucible lined with magnesia, and extracting the cold mass with water.

Mercury Tungstates. Normal mercurous tungstate, Hg_2WO_4, is formed as a yellow precipitate by mixing a soluble mercurous salt and alkali tungstate. When dried, it is dark yellow, and after ignition, tungstic anhydride remains. Normal mercuric tungstate, $HgWO_4$, is precipitated as a light-yellow product by adding a neutral solution of mercuric acetate to a saturated solution of sodium tungstate.

Neodymium Tungstate is obtained by adding neodymium chloride to a solution of sodium tungstate. The gelatinous precipitate thus formed changes, on ignition, from pale rose to lavender.

Nickel Tungstate, $NiWO_4$, is obtained in well-defined brown, lustrous, translucent, rhombic prisms, by fusing a mixture of sodium tungstate, and nickel and sodium chlorides (1:2:2). The trihydrate, $NiWO_4 \cdot 3H_2O$, and the hexahydrate, $NiWO_4 \cdot 6H_2O$, are obtained as a light-green powder by precipitation from mixtures of solution of normal potassium tungstate and a nickel salt.

Potassium Tungstates. The anhydrous normal salt, K_2WO_4, is prepared by crystallization from a fusion mixture of tungstic anhydride and potassium hydroxide or carbonate, or from a filtered solution of tungstic acid in solution of potassium hydroxide or carbonate.

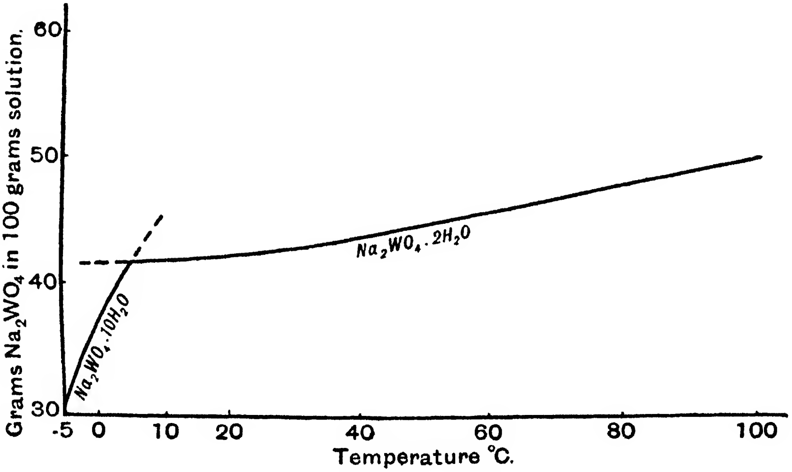
The solution of normal potassium tungstate is strongly alkaline in reaction.

The dihydrate, $K_2WO_4 \cdot 2H_2O$, and the pentahydrate, $K_2WO_4 \cdot 5H_2O$, have been described.

Praseodymium Tungstate is obtained as a greenish-yellow, gelatinous precipitate on treating a solution of sodium tungstate with a solution of praseodymium chloride.

Silver Tungstates. The normal salt, Ag_2WO_4, is obtained as a fine yellow precipitate by treating a solution of sodium tungstate with silver nitrate. It is slightly soluble in water and melts below redness to form a dark-red liquid. A mixture of silver tungstate and metallic silver has been known as "argentous" tungstate. Silver tetraammoniotungstate, $Ag_2WO_4 \cdot 4NH_3$, is obtained as a white powder by the action of ammonia gas on silver tungstate, but, when heated to over 60°, it gives up all the ammonia.

Sodium Tungstates. Anhydrous sodium tungstate is obtained by fusing together equal proportions of tungsten trioxide and the alkali hydroxide or carbonate, or by complete dehydration of the hydrates at 100° or over sulfuric acid. The preparation of the salt has been discussed in connection with the metallurgical treatment of wolframite.



Solubility of sodium tungstate. *After J. Newton Friend*

Anhydrous sodium tungstate is obtained as white crystals and, when heated, undergoes two transformations. The transition temperatures between the polymorphic forms are as follows:

Authorities	Transition Point $\delta \rightleftharpoons \gamma$ (°C)	Transition Point $\gamma \rightleftharpoons \beta$ (°C)	Melting point of β Form (°C)
Hüttner and Tammann	570	. . .	698
Boeke	564	588	698
Parravano	568	585	698
van Klooster	572	589	700
van Klooster and Germs	587	591	694

The relation of sodium tungstate to water, that is, its solubility, was found by R. Funk to be as follows:

	−5°	0°	5°	6°	10°	20°	40°	80°	100°
Percentage Solubility	30.6	36.5	41.0	41.8	41.9	42.2	43.8	47.4	49.2
	$10H_2O$			$2H_2O$					

The dihydrate, $Na_2WO_4 \cdot 2H_2O$, may be obtained from a solution of tungsten trioxide and sodium carbonate, of the oxide and sodium hydroxide, or from an aqueous solution of a previously melted mixture of wolframite and sodium carbonate. The aqueous solution, when allowed to crystallize at temperatures above 6°, yields slender nacreous crystals of the dihydrate in the form of rhombic bipyramidal scales, of density 3.259 at 17.5° and 3.231 at 19°. The dihydrate is stable in the air and loses water at 200°. On the addition of mineral acids, the aqueous solution of the dihydrate yields white tungstic acid. It readily dissolves in hot water, but may be precipitated with alcohol.

The aqueous solution, when cooled below 6°, furnished the decahydrate, $Na_2WO_4 \cdot 10H_2O$.

The density of the anhydrous salt is 4.1833 at 18.5° and 4.1743 at 20.5° and that of the dihydrate is 3.2588 at 17.5° and 3.2314 at 18.5°. The melting point of sodium tungstate is 698°.

The heat of formation is as follows:—

$$W + 3Na_2O_2 = Na_2WO_4 + 2Na_2O + 231.2 \text{ Cals}$$
$$W + Na_2O + 3O = Na_2WO_4 + 291 \text{ Cals}$$
$$WO_3 + Na_2O = Na_2WO_4 + 94.1 \text{ Cals}$$
$$H_2WO_4 \cdot xH_2O + 2NaOH \cdot xH_2O = Na_2WO_4 \cdot xH_2O + H_2O + 13.694 \text{ Cals}$$

Strontium Tungstate, $SrWO_4$, is obtained by mixing a solution of a strontium salt with normal potassium or sodium tungstate; or it may be obtained in the crystalline form by fusing together strontium chloride, sodium tungstate, and sodium chloride. The crystals are white, translucent, tetragonal bipyramids, of density 6.184. The salt is easily decomposed when heated.

Thallium Tungstate. The normal thallous tungstate, Tl_2WO_4, is obtained by mixing a solution of normal sodium tungstate and a thallous salt, or by boiling tungstic acid with thallous carbonate. The salt is insoluble in water, but is soluble in hot solution of alkali hydroxide or carbonate.

Thorium Tungstate. A white flocculent precipitate of thorium tungstate is formed when a solution of a thorium salt is treated with sodium tungstate.

Tin Tungstate. Stannous tungstate, $SnWO_4 \cdot 6H_2O$, is obtained by mixing solutions of sodium tungstate and stannous chloride. The powder thus produced is yellowish in color.

Uranium Tungstate. Uranyl tungstate, UO_2WO_4, is formed as a pale-yellow precipitate when a solution of a uranyl salt is treated with a soluble tungstate. Uranium tungstate, $U(WO_4)_3 \cdot 5H_2O$, is formed as a yellow precipitate by treating uranyl acetate with sodium ditungstate; when normal sodium tungstate is employed, the dihydrate, $UO_2(WO_4) \cdot 2H_2O$, is formed. When ammonium tungstate is treated with a solution of uranium tetrachloride, a brownish-green precipitate of composition $U(WO_4)_2 \cdot WO_3 \cdot 6H_2O$ is obtained.

Ytterbium Tungstate. By fusing a mixture of ytterbium oxide and sodium tungstate and chloride, and extracting the mass with water, two products are obtained: ytterbium oxytungstate, $Yb_2O_3 \cdot WO_3$ or $(YbO)_2WO_4$, and sodium ytterbium tungstate, $4Na_2O \cdot 2Yb_2O_3$.

Zinc Tungstate. The anhydrous normal salt, $ZnWO_4$, is obtained as rhombic crystals by melting together sodium tungstate, sodium chloride and zinc chloride in proportions 1:2:2. The monohydrate, $ZnWO_4 \cdot H_2O$, is formed by double decomposition as in the case of calcium hydrate. The product is slightly soluble in water.

The Ditungstates and Tritungstates

Ammonium Tritungstate, $2(NH_4)_2O \cdot 3WO_3 \cdot 3H_2O$. From a very concentrated neutral solution of tungstic acid in ammonia, the acid tungstate is obtained as crystals, which give off ammonia in contact with air, leaving the paratungstate.

Barium Ditungstate, $BaO \cdot 2WO_3 \cdot H_2O$, may be formed by double decomposition from solutions of sodium ditungstate and barium acetate. It is a white amorphous precipitate, slightly soluble in water.

Cadmium Tritungstate, $CdO \cdot 3WO_3 \cdot 4H_2O$. By mixing solutions of cadmium acetate and sodium tritungstate, a white translucent gummy mass of the tritungstate is obtained.

Calcium Ditungstate, $CaO \cdot 2WO_3$, is obtained as a white precipitate by treating a solution of calcium acetate with sodium ditungstate at 15°. If the mother-liquor is concentrated by evaporation, the crystals obtained are presumed to be the dihydrate.

Calcium Tritungstate, $CaO \cdot 3WO_3 \cdot 6H_2O$. According to J. Lefort, the tritungstate may be obtained by mixing concentrated solutions of sodium tritungstate and calcium acetate or calcium chloride. Decomposition of the precipitate by hot water yields the di- and meta-tungstates.

Cerium Tritungstate, $CeO \cdot 3WO_3$, is obtained by igniting the pale-yellow precipitate produced from a mixture of solutions of cerium sulfate and sodium tungstate.

Cobalt Ditungstate, $CoO \cdot 2WO_3 \cdot 3H_2O$, is obtained as a reddish-brown precipitate by double decomposition.

Cobalt Tritungstate, $CoO \cdot 3WO_3 \cdot 4H_2O$, has been investigated by J. Lefort.

Cupric Ditungstate, $CuO \cdot 2WO_3 \cdot 4H_2O$, may be obtained as a light-green precipitate when a cupric salt is added to a ditungstate solution.

Indium Tritungstate, $In_2O \cdot 3WO_3 \cdot 8H_2O$, is obtained by adding a solution of sodium tungstate to one of an indium salt.

Ferrous Ditungsiate, $FeO \cdot 2WO_3 \cdot 2H_2O$, is formed as a cinnamon-brown precipitate, when a ferrous salt is added to a solution of sodium ditungstate.

Ferric Di- and Tri-tungstates, $Fe_2O_3 \cdot 2WO_3 \cdot 4H_2O$ and $2Fe_2O_3 \cdot 3WO_3 \cdot 6H_2O$, as described by J. Lefort, may be obtained as yellow precipitates by adding a solution of normal or acid sodium tungstate to one of ferric acetate. They may be formed on the addition of a ferric salt to a solution of ammonium tungstate.

Lead Ditungstate, $PbO \cdot 2WO_3 \cdot 2H_2O$, is obtained as a white precipitate by mixing a solution of lead acetate and sodium ditungstate.

Magnesium Ditungstate, $MgO \cdot 2WO_3 \cdot 8H_2O$, is prepared by crystallizing a heated mixture of suspended magnesium hydroxide with excess of tungstic acid.

Magnesium Tritungstate, $MgO \cdot 3WO_3 \cdot 4H_2O$, is obtained by pouring a mixed solution of magnesium acetate and sodium tritungstate into alcohol.

Manganese Tritungstate, $MnO \cdot 3WO_3 \cdot 5H_2O$, is obtained by double decomposition in presence of alcohol.

Mercuric Ditungstate, $3HgO \cdot 2WO_3$. This basic salt is obtained when a boiling solution of mercuric chloride is treated with an insufficient quantity of alkali tungstate.

Mercuric Tritungstate, $2HgO \cdot 3WO_3$, is obtained as a white insoluble powder by treating a solution of mercuric nitrate with normal sodium tungstate. The heptahydrate, $HgO \cdot 3WO_3 \cdot 7H_2O$, is obtained by pouring a solution of 2 equivalent of sodium ditungstate into a saturated solution of an equivalent of mercuric chloride, and allowing the solution to crystallize.

Mercurous Tritungstate, $2Hg_2O \cdot 3WO_3 \cdot 8H_2O$, is prepared by dissolving mercurous nitrate, by the aid of glycerol, in water, and mixing the filtered solution with a concentrated solution of sodium ditungstate. The pale yellow precipitate loses water when warmed.

Nickel Ditungstate and Tritungstate. The salts, $NiO \cdot 2WO_3 \cdot 5H_2O$, $NiO \cdot 2WO_3 \cdot 7H_2O$, and $NiO \cdot 3WO_3 \cdot 4H_2O$ have been described by J. Lefort.

Potassium Ditungstate, $K_2O \cdot 2WO_3 \cdot 2H_2O$, is formed when acetic or oxalic acid is gradually poured into a cold concentrated solution of potassium tungstate.

Potassium Tritungstate, $K_2O \cdot 3WO_3 \cdot 2H_2O$, is obtained by pouring a concentrated solution of the normal salt into a boiling solution of acetic acid. The resulting white precipitate must be immediately filtered and washed with alcohol; otherwise the metatungstate is formed.

The double tungstate, $K_2Na_4(WO_4)_3$, has been obtained byUllik.

Sodium Ditungstate, $Na_2O \cdot 2WO_3$, is obtained by melting a mixture of a mol of sodium carbonate or sodium hydroxide and 2 moles of tungstic anhydride. It dissolves completely when heated for some time with water at 130° to 150°, yielding an alkaline solution containing sodium tungstate and metatungstate.

The dihydrate, $Na_2O \cdot 2WO_3 \cdot 2H_2O$, is obtained by adding hydrochloric acid to a solution of the normal tungstate. The hexahydrate, $Na_2O \cdot 2WO_3 \cdot 6H_2O$ and the dodecahydrate, $Na_2O \cdot 2WO_3 \cdot 12H_2O$, have been described.

Strontium Ditungstate, $SrO \cdot 2WO_3 \cdot 3H_2O$, may be formed as a white precipitate by the addition of strontium acetate to sodium ditungstate solution.

Uranium Tritungstate, $(UO_2)3WO_3 \cdot 6H_2O$, is obtained as a brownish-green precipitate by adding ammonium tungstate to an aqueous solution of uranium tetrachloride.

Zinc Ditungstate, $ZnO \cdot 2WO_3 \cdot 3H_2O$, is obtained as crystals by concentrating a mixed solution of a zinc salt and sodium ditungstate.

Zinc Tritungstate, $ZnO \cdot 3WO_3 \cdot 5H_2O$, is known.

The Paratungstates

Aluminum Paratungstate, $Al_2O_3 \cdot 7WO_3 \cdot 9H_2O$, is formed as a white caseous precipitate by mixing a solution of ammonium paratungstate and an aluminum salt.

Ammonium Paratungstate, $5(NH_4)_2O \cdot 12WO_3 \cdot 11H_2O$, or $3(NH_4)_2O \cdot 7WO_3 \cdot 6H_2O$, is obtained by the interaction of tungstic acid and ammonia or by concentrating an ammoniacal solution of normal ammonium tungstate. Its preparation has been discussed under "II. 2. Crystallization as Ammonium Tungstate", in Chapter IV.

The paratungstate is dimorphous, yielding acicular needles if slowly crystallized, and laminated plates if rapidly crystallized. The salt loses 2.15 per cent of water at 100° while ammonia begins to come off at 60°. By boiling the salt in aqueous solution for several days, the metatungstate is formed.

The pentahydrate, $5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$, may be formed by evaporation of a solution of the paratungstate at temperatures near the boiling point. The hexahydrate, $5(NH_4)_2O \cdot 12WO_3 \cdot 6H_2O$, is obtained by the addition of acetic acid to a solution of ammonium tungstate.

Barium Paratungstate, $3BaO \cdot 7WO_3 \cdot xH_2O$, is obtained by adding an excess of a barium salt to a solution of an alkali paratungstate. The H_2O content in the salt depends upon the temperature of its exposure. The double salt, $3Na_2O \cdot 2BaO \cdot 12WO_3 \cdot 24H_2O$ or $2Na_2O \cdot BaO \cdot 7WO_3 \cdot 14H_2O$, is formed by cooling a boiling solution of sodium paratungstate to which an excess of barium hydroxide solution is added.

Cadmium Paratungstate, $3CdO \cdot 7WO_3 \cdot 16H_2O$, is prepared by mixing hot solutions of an alkali paratungstate and a cadmium salt. The white crystals are infusible and turn orange after heating. The double salt, $2CdO \cdot Na_2O \cdot 7WO_3 \cdot 18H_2O$, may be prepared from solutions containing molecular proportions of sodium paratungstate and cadmium sulfate at 18°.

Calcium Paratungstate, $3CaO \cdot 7WO_3 \cdot 18H_2O$. Treatment of a solution of sodium paratungstate with an excess of calcium chloride yields a white precipitate, which when digested with the mother liquor, washed and dried, is obtained as calcium paratungstate. According to C. Gonzalez, if the aqueous solution of calcium chloride is so added that the precipitate first formed no longer dissolves and the slightly turbid solution is rapidly filtered, the double salt, $3Na_2O \cdot 2CaO \cdot 12WO_3 \cdot 34H_2O$, is formed.

Cerium Paratungstate. The double tungstate of sodium and cerium, $4Na_2O \cdot Ce_2O_3 \cdot 7WO_3$ or $Na_8Ce_2(WO_4)_7$, is prepared by adding a mixture of cerium dioxide and tungsten anhydride to a fused mixture of sodium chloride and sodium tungstate, the latter being in excess.

Chromium Paratungstate, $CrO_3 \cdot 7WO_3 \cdot xH_2O$, is prepared by mixing solutions of sodium paratungstate and chromic chloride. The greyish-green precipitate, when dried at 100° after calcination loses 9 mols of water. The compounds $Cr_2O_3 \cdot 5WO_3$, $Cr_2O_3 \cdot 5WO_3 \cdot 5H_2O$, $Cr_2O_3 \cdot 4WO_3 \cdot 6H_2O$, $Cr_2O_3 \cdot 3WO_3 \cdot 3H_2O$, and $Cr_2O_3 \cdot 2WO_3 \cdot 5H_2O$, appear to be either identical with the paratungstate or mixtures of the para- and metatungstates.

Cobalt Paratungstate, $3CoO \cdot 7WO_3 \cdot 25H_2O$, is prepared by mixing solutions of sodium paratungstate and a cobalt salt. The bright-rose precipitate does not melt at red heat, but on cooling shows a bluish tinge.

The following double salts are known: $3Na_2O \cdot 2CoO \cdot 12WO_3 \cdot 30H_2O$, $2Na_2O \cdot 3CoO \cdot 12WO_3 \cdot 41H_2O$, and $Na_2O \cdot 4CoO \cdot 12WO_3 \cdot 23H_2O$.

Copper Paratungstate, $3CuO \cdot 7WO_3 \cdot 19H_2O$ or $5CuO \cdot 12WO_3 \cdot 33H_2O$, is formed on the addition of excess copper sulfate to a solution of sodium paratungstate at 17°. The light blue or bluish-green precipitate becomes yellow after heating. The double salt $4Na_2O \cdot CuO \cdot 12WO_3 \cdot 32H_2O$ has been described.

Lanthanum Paratungstate. The double tungstate of sodium and lanthanum, $4Na_2O \cdot La_2O_3 \cdot 7WO_3$, may be obtained by dissolving lanthanum oxide and tungstic acid in fused sodium tungstate.

Lead Paratungstate, $3PbO \cdot 7WO_3 \cdot 10H_2O$, is formed as a white precipitate on adding a solution of lead nitrate to one of ammonium paratungstate. The double tungstate of sodium and lead, $4Na_2O \cdot PbO \cdot 12WO_3 \cdot 28H_2O$, is obtained by adding a solution of lead salt to a boiling solution of sodium paratungstate.

Lithium Paratungstate, $5Li_2O \cdot 12WO_3 \cdot 33H_2O$ or $3Li_2O \cdot 7WO_3 \cdot 19H_2O$, is prepared by adding tungstic acid to a solution of lithium carbonate until the mixture is neutral to litmus and evaporating the product slowly over sulfuric acid. It crystallizes as rhombic plates or prisms.

Magnesium Paratungstate, $3MgO \cdot 7WO_3 \cdot 24H_2O$, is obtained by adding a solution of a mol of sodium paratungstate to a solution of 3 mols of magnesium sulfate. The white, crystalline powder is slightly soluble in cold water, more soluble in hot water, and is decomposed by acids. The double salts, $2(NH_4)_2O \cdot 3MgO \cdot 12WO_3 \cdot 24H_2O$ and $(NH_4)_2O \cdot 2MgO \cdot 7WO_3 \cdot 10H_2O$, have been described.

Manganese Paratungstate, $3MnO \cdot 7WO_3 \cdot 20H_2O$ or $5MnO \cdot 12WO_3 \cdot 34H_2O$, is precipitated by adding sodium paratungstate to a manganous salt. The white precipitate has a yellowish tinge, which becomes yellow after ignition. The double salts, $3K_2O \cdot 2MnO \cdot 12WO_3 \cdot 16H_2O$ and $4(NH_4)_2O \cdot Mn_2O_3 \cdot 12WO_3 \cdot 23H_2O$, have been described.

Nickel Paratungstate, $3NiO \cdot 7WO_3 \cdot 14H_2O$, is obtained as a light-green precipitate by mixing solutions of a nickel salt and an acid tungstate of sodium.

Platinum Paratungstate. The complex salt $5NaO \cdot 2PtO_2 \cdot 7WO_3 \cdot 35H_2O$, may be prepared by boiling platinic hydroxide in a solution of an alkaline tungstate. Probably this complex salt is a double salt of sodium paratungstate and sodium platinate, $3Na_2O \cdot 7WO_3 + 2(Na_2O \cdot PtO_2) \cdot 35H_2O$.

Potassium Paratungstate, $5K_2O \cdot 12WO_3 \cdot 11H_2O$ or $3K_2O \cdot 7WO_3 \cdot 6H_2O$, may be formed by boiling sodium decatungstate with potassium bromide or nitrate by adding acetic acid to a cold concentrated solution of the normal tungstate and boiling the resulting precipitate with water, or by fusing together tungstic anhydride with potassium carbonate or potassium tungstate and lixiviating the fused mass. The salt is somewhat soluble in cold water, but dissolves readily in hot water. When heated red-hot it fuses, undergoing decomposition, and on cooling sets to a yellow crystalline mass.

Rubidium Paratungstate, $5Rb_2O \cdot 12WO_3 \cdot 18H_2O$, is obtained by fusing an equimolar mixture of rubidium carbonate and tungsten anhydride, extracting the cold product with water and by boiling the liquid with enough hydrochloric acid to prevent blue litmus from becoming red.

Silver Paratungstate, $5Ag_2O \cdot 12WO_3 \cdot 28H_2O$, is obtained on adding a solution of a silver salt to a solution of sodium paratungstate. The whitish-yellow crystalline precipitate melts at red heat.

Sodium Paratungstate, $5Na_2O \cdot 12WO_3 \cdot xH_2O$ or $3Na_2O \cdot 7WO_3 \cdot xH_2O$, is manufactured by fusing wolframite with soda ash, lixiviating the product with water and nearly neutralizing the boiling solution with hydrochloric acid. It may be formed by saturation of a solution of sodium hydroxide, carbonate, or tungstate, with anhydrous tungstic acid, by addition of a solution of sodium metatungstate to one of the normal tungstate, or by saturation of a solution of normal sodium tungstate with carbon dioxide.

The five hydrates, showing distinctive properties, as to their solubility, crystalline form, etc. are:

(1) The octocosihydrate, $5Na_2O \cdot 12WO_3 \cdot 28H_2O$, is formed when crystallization takes place at ordinary temperatures, or lower. Its crystal habit is triclinic pinacoidal, and its density is 3.987 at 14°. On heating, the salt loses water. At red heat it melts, forming a crystalline mass, which upon lixiviation yields the insoluble residue of the tetratungstate, $Na_2O \cdot 4WO_3$. According to von Knorre, the decomposition may be represented thus:

$$3(5Na_2O \cdot 12WO_3) \rightarrow 7(Na_2O \cdot 4WO_3) + 8(Na_2O \cdot WO_3)$$

The solubility of the paratungstate is 1 in 8 or 12 parts of cold water.

If the paratungstate is boiled with water or is kept for a considerable length of time in aqueous solution, it is decomposed into the normal and metatungstates.

(2) The pentacosihydrate, $5Na_2O \cdot 12WO_3 \cdot 25H_2O$, is formed when crystallization takes place at about 60 to 80°. It crystallizes as monoclinic prisms. When heated to 100°, it loses 9.15 per cent water.

(3) The henicosihydrate, $5Na_2O \cdot 12WO_3 \cdot 21H_2O$, is formed when crystallization takes place at 100°. The crystals thus obtained are octahedra of the triclinic system.

(4) The hexadecahydrate, $3Na_2O \cdot 7WO_3 \cdot 16H_2O$, is obtained by crystallization from a solution of a paratungstate containing sodium carbonate. The crystals are of short prisms, triclinic pinacoids.

(5) The henicosihydrate, $3Na_2O \cdot 7WO_3 \cdot 21H_2O$, is obtained by boiling an aqueous solution of sodium paratungstate for a long time. The crystals are of short prisms, triclinic pinacoids.

Strontium Paratungstate, $3SrO \cdot 7WO_3 \cdot 16H_2O$, is formed on adding a hot solution of a paratungstate to a hot solution of strongium chloride or nitrate, the strontium salt being in excess. The double salt, $Na_2O \cdot 4SrO \cdot 12WO_3 \cdot 29H_2O$, has been described.

Thallous Paratungstate, $5Tl_2O \cdot 12WO_3 \cdot 9H_2O$, is prepared by adding excess of thallous sulfate solution to a solution of sodium paratungstate.

Zinc Paratungstate, $5ZnO \cdot 12WO_3 \cdot 37H_2O$, is prepared by the addition of a zinc salt to a solution of sodium paratungstate. The double tungstate of ammonium and zinc, $(NH_4)_2O \cdot 2ZnO \cdot 7WO_3 \cdot 13H_2O$, has been prepared.

The Metatungstates and Tetratungstates

Investigation of the water content of the metatungstate has led to the conclusion that apart from water of crystallization there may be present water of constitution. The difference between the metatungstate and the tetratungstate is that the latter is anhydrous.

Most of the metatungstates, with the exception of the lead and mercurous salts, are soluble in water. The method for the preparation of potassium metatungstate is applicable to all other alkali salts; other metatungstates may be prepared by adding the sulfate of the metal to a solution of barium metatungstate, or by neutralizing metatungstic acid with the oxide or carbonate. The metatungstates can crystallize only after prolonged evaporation in the cold.

Ammonium Metatungstates, the octahydrate, $(NH_4)_2O \cdot 4WO_3 \cdot 8H_2O$, is prepared by dissolving in water and allowing to crystallize the residue obtained by prolonged heating of crystalline ammonium paratungstate at 250°, and by boiling a solution of ammonium paratungstate for several days and then allowing to crystallize.

The salt crystallizes in large, lustrous, tetragonal octahedra, loses water of crystallization at 100°, begins to lose ammonia at 120° and coalesces at 250° into a glass-like colloidal tungstate of composition, $(NH_4)_2W_6O_{19} \cdot 4$ or $6H_2O$. It is soluble in water.

The hexahydrate, $(NH_4)_2O \cdot 4WO_3 \cdot 6H_2O$, is obtained by treating a hot solution of the salt with alcohol. It crystallizes in monoclinic prisms.

Barium Metatungstate, $BaO \cdot 4WO_3 \cdot 9H_2O$, or $Ba_3H_4\ H_2(W_2O_7)_6\ 25H_2O$, is obtained by mixing boiling solutions of sodium metatungstate and barium chloride in the presence of a few drops of hydrochloric acid and allowing to cool. The resulting crystals are contaminated with some tritungstate, which can be removed by recrystallization. The crystals are lustrous, milky-white, rhombic bipyramids. The density of the salt is 4.298 at 14°. The salt is decomposed by water, and, when heated to 100°, loses two-thirds of its water.

Beryllium Metatungstate may be obtained, according to C. Scheibler, by double decomposition with beryllium sulfate and barium metatungstate. The resulting product is in fine laminae and is very deliquescent.

Cadmium Metatungstate, $CdO \cdot 4WO_3 \cdot 10H_2O$, is formed by the addition of barium metatungstate to a solution of cadmium sulfate. The resulting crystals are octahedral. The salt is stable in the aid but loses $7H_2O$ on heating at 100 to 110°.

Calcium Metatungstate, $CaO \cdot 4WO_3 \cdot 10H_2O$, is obtained by digesting hot metatungstic acid with calcium carbonate. It crystallizes with difficulty, yielding triclinic pinacoidal crystals.

Cerium Metatungstate, $CeO \cdot 4WO_3 \cdot 30H_2O$, crystallizes in triclinic pinacoidal prisms and is stable in air at ordinary temperatures.

Cobalt Metatungstate, $CoO \cdot 4WO_3 \cdot 9H_2O$, is obtained by double decomposition with solution of cobaltous sulfate and barium metatungstate. The crystals are rhombic bipyramids.

Copper Metatungstate, $CuO \cdot 4WO_3 \cdot 11H_2O$, is obtained by mixing solutions of barium metatungstate and copper sulfate. Copper hexamminometatungstate, $CuO \cdot 4WO_3 \cdot 6NH_3 \cdot 8H_2O$, has been prepared.

Ferrous Metatungstate is prepared by dissolving iron in metatungstic acid. Iron tetratungstate, $Fe_2O_3 \cdot 4WO_3 \cdot 4H_2O$, has been described by Lefort.

Lead Metatungstate, $PbO \cdot 4WO_3 \cdot 5H_2O$, is obtained as a white flocculent precipitate from solutions of lead acetate and metatungstic acid. It is insoluble in water but soluble in hot nitric acid. Lead nitratometatungstate, $Pb(NO_3)_2 \cdot PbO(WO_3)_4 \cdot 10H_2O$, is formed by the addition of lead nitrate to an alkali tungstate solution.

Lead Tetratungstate, $3PbO \cdot 4WO_3$, is formed by adding a solution of lead acetate to one of sodium tungstate, washing with water and alcohol and drying over quicklime and sulfuric acid.

Lithium Tetratungstate, $Li_2O \cdot 4WO_3$, is formed on washing well with water the mass obtained by fusing together lithium carbonate (5 molecules) and tungsten trioxide (12 molecules).

Magnesium Metatungstate, $MnO \cdot 4WO_3 \cdot 10H_2O$, is obtained by double decomposition with solutions of barium metatungstate and manganous sulfate. It forms beautiful light-yellow quadratic octahedra. On heating at 100 to 110° it loses $7H_2O$, while the remaining $3H_2O$ can only be expelled at a much higher temperature.

Mercurous Metatungstate, $Hg_2O \cdot 4WO_3 \cdot 25H_2O$, is formed by adding a solution of mercurous nitrate to one of an alkaline metatungstate; it gives a white precipitate, which assumes a lemon-yellow color on drying.

Mercurous Nitratometatungstate, $9H_2O \cdot 24WO_3 \cdot Na_2O_5 \cdot 29H_2O$, has been described.

Nickel Metatungstate, $NiO \cdot 4WO_3 \cdot 8H_2O$, is formed by double decomposition and yields monoclinic prisms.

Potassium Metatungstate, $K_2O \cdot 4WO_3 \cdot xH_2O$, may be prepared by boiling a solution of the paratungstate with excess of tungstic anhydride until the filtered solution no longer gives a precipitate with hydrochloric acid, and then allowing the concentrated solution to crystallize slowly over sulfuric acid. It may also be prepared by adding a large excess of acetic acid to a saturated solution of potassium paratungstate, or by adding a concentrated mineral acid solution to the paratungstate solution until the precipitate no longer redissolves. The octohydrate, $K_2O \cdot 4WO_3 \cdot 8H_2O$, and the pentahydrate, $K_2O \cdot 4WO_3 \cdot 5H_2O$, have been reported.

Rubidium Metatungstate, $Rb_2O \cdot 4WO_3 \cdot 8H_2O$, is formed by mixing solutions of barium metatungstate and rubidium sulfate. The crystals lose water when exposed to air.

Samarium Metatungstate, $Sa_2O \cdot 4WO_3 \cdot 35H_2O$, is formed by double decomposition. The crystals are readily soluble in water.

Silver Metatungstate, $Ag_2O \cdot 4WO_3 \cdot 3H_2O$, is prepared by boiling solutions of sodium metatungstic and silver nitrate in the presence of a little nitric acid. The white scaly crystals lose 0.65 mol of water at 110°, 0.87 mol at 150°, 1.1 mols at 160° and 1.3 mols at 200°.

Sodium Metatungstate, $Na_2O \cdot 4WO_3 \cdot 10H_2O$, is obtained by methods analogous to those described for potassium metatungstate. It crystallizes in colorless, glistening tetragonal bipyramids. The crystals are very efflorescent and lose most of their water if placed over sulfuric acid. The salt appears yellow when heated, and on cooling, bluish-grey. When heated it loses $7H_2O$ per molecule at 120° and at 240° only 1 H_2O remains. If the ignited salt is extracted with water, normal sodium tungstate passes into solution. The solubility of the salt in water at ordinary temperature is 10.69 parts to 1 part respectively.

Sodium Tetratungstate, $Na_2O \cdot 4WO_3$, is obtained by the complete dehydration of the metatungstate. It is insoluble in water, but if heated with water at 120°, it is converted into the metatungstate.

Strontium Metatungstate, $SrO \cdot 4WO_3 \cdot 8H_2O$, is prepared by adding strontium carbonate in excess to a hot solution of metatungstic acid.

Thallous Metatungstate, $Tl_2O \cdot 4WO_3 \cdot 3H_2O$, is obtained by method analogous to that described for silver salt.

Zinc Metatungstate, $ZnO \cdot {}_4WO_3 \cdot 10H_2O$, is obtained by the addition of zinc sulfate to a solution of the barium salt.

The Higher Tungstates

The higher tungstates play a minor role in the compounds of tungsten and oxygen. They have been described and are tabulated below for reference.

The Pentatungstates:

Aluminum:	$Al_2O_3 \cdot 5WO_3 \cdot 6H_2O$
Ammonium:	$2(NH_4)_2O \cdot 5WO_3 \cdot 5H_2O$, $3NH_4OH \cdot 5WO_3$
Antimony:	$Sb_2O_3 \cdot 5WO_3 \cdot 4H_2O$
Chromium:	$Cr_2O_3 \cdot 5WO_3$
Mercury:	$3HgO \cdot 5WO_3 \cdot 5H_2O$
Potassium:	$2K_2O \cdot 5WO_3 \cdot 4H_2O$
Rubidium:	$Rb_2O \cdot 5WO_3$
Sodium:	$Na_2O \cdot 5WO_3$
Zinc:	$2ZnO \cdot 5WO_3 \cdot 9H_2O$

The Hexatungstates:

Ammonium:	$(NH_4)_2O \cdot 6WO_3 \cdot 4$ or 6 H_2O
Potassium:	$K_2O \cdot 6WO_3 \cdot xH_2O$
Sodium:	$Na_2O \cdot 6WO_3 \cdot 15H_2O$

The Octatungstates:

Ammonium:	$3(NH_4)_2O \cdot 8WO_3 \cdot 8H_2O$
Ammonium and Sodium:	$3[(NH_4)Na]_2O \cdot 8WO_3 \cdot 11H_2O$

Barium:	$BaO \cdot 8WO_3 \cdot 8H_2O$
Potassium:	$K_2O \cdot 8WO_3$
Potassium Uranium:	$9K_2O \cdot 6UO_2 \cdot 8WO_3 \cdot 34H_2O$
Rubidium:	$Rb_2O \cdot 8WO_3$
Sodium:	$Na_2O \cdot 8WO_3$
Sodium Uranium:	$12Na_2O \cdot 6UO_2 \cdot 8WO_3 \cdot 25H_2O$

The Nonatungstates:

Ammonium Alumino:	$3(NH_4)_2O \cdot Al_2O_3 \cdot 9WO_3 \cdot 4H_2O$
Barium Alumino:	$8BaO \cdot Al_2O_3 \cdot 9WO_3 \cdot 7H_2O$
Copper Alumino:	$2CuO \cdot Al_2O_3 \cdot 9WO_3 \cdot 16\frac{1}{2}H_2O$
Mercurous Alumino:	$5Hg_2O \cdot Al_2.O_3 \cdot 9WO_3$
Silver Alumino:	$11Ag_2O \cdot 21(NH_4)_2O \cdot 4Al_2O_3 \cdot 36WO_3$
Zinc Alumino:	$1\frac{1}{2}ZnO \cdot Al_2O_3 \cdot 9WO_3 \cdot 8H_2O$ $ZnO \cdot Al_2O_3 \cdot 9WO_3 \cdot 20H_2O$
Zirconium:	$5ZrO_2 \cdot 9WO_3 \cdot 33H_2O$
Alumino-phosphotungstates:	$9(NH_4)_2O \cdot 2Al_2O_3 \cdot 4P_2O_5 \cdot 9WO_3 \cdot 13H_2O$ $4BaO \cdot 2Al_2O_3 \cdot 4P_2O_5 \cdot 9WO_3 \cdot 3H_2O$ $4Ag_2O \cdot 2Al_2O_3 \cdot 4P_2O_5 \cdot 9WO_3 \cdot 6H_2O$ $5ZnO \cdot 2Al_2O_3 \cdot 4P_2O_5 \cdot 9WO_3 \cdot 11H_2O$

The Decatungstates:

Ammonium:	$4[4(NH_4)_2O \cdot 10WO_3] \cdot 4Na_2O \cdot 10WO_3 \cdot 50H_2O$, $3(NH_4)_2O \cdot Na_2O \cdot 10WO_3 \cdot 12H_2O$
Ammonium Zirconium:	$3(NH_4)_2O \cdot ZrO_2 \cdot 10WO_3 \cdot 14H_2O$
Barium:	$4BaO \cdot 10WO_3 \cdot 22H_2O$
Calcium:	$4CaO \cdot 10WO_3 \cdot 25H_2O$
Cobalt:	$4CoO \cdot 10WO_2 \cdot 35H_2O$
Manganese:	$4MnO \cdot 10WO_3 \cdot 30H_2O$
Nickel:	$4NiO \cdot 10WO_3 \cdot 34H_2O$
Potassium Ferric:	$3K_2O \cdot Fe_2O_3 \cdot 10WO_3 \cdot 23H_2O$
Strontium:	$4SrO \cdot 10WO_3 \cdot 26H_2O$

The Dodecatungstates:

Ammonium Ferric:	$4(NH_4)_2O \cdot Fe_2O_3 \cdot 12WO_3 \cdot 23H_2O$
Potassium Ferric:	$K_4H_5[Fe(WO_4)_6] \cdot 9H_2O$
Samarium:	$Sa_2O_3 \cdot 12WO_3 \cdot 35H_2O$

The Tetradecatungstates:

Potassium:	$5K_2O \cdot 14WO_3$

The Pentadecatungstates:

Ammonium Sodium:	$3(NH_4)_2O \cdot 2Na_2O \cdot 15WO_3 \cdot 25H_2O$, $4(NH_4)_2O \cdot 2Na_2O \cdot 15WO_3 \cdot 21H_2O$

The Hexadecatungstates:
Ammonium: $3(NH_4)_2O \cdot 16WO_3 \cdot 17H_2O$
Ammonium Sodium: $4(NH_4)_2O \cdot 3Na_2O \cdot 16WO_3 \cdot 18H_2O$
Ammonium Cerous: $2(NH_4)_2O \cdot Ce_2O_3 \cdot 16WO_3 \cdot 2H_2O$
Ammonium Lanthanum: $2(NH_4)_2O \cdot La_2O_3 \cdot 16WO_3 \cdot 16H_2O$
Ammonium Praseodymium: $2(NH_4)_2O \cdot Pr_2O_3 \cdot 16WO_3 \cdot 16H_2O$
Barium Lanthanum: $5BaO \cdot La_2O_3 \cdot 16WO_3 \cdot 16H_2O$
Barium Neodymium: $6BaO \cdot Nd_2O_3 \cdot 16WO_3 \cdot 17H_2O$
Barium Praseodymium: $4BaO \cdot Pr_2O_3 \cdot 16WO_3 \cdot 7H_2O$
Silver Lanthanum: $5Ag_2O \cdot La_2O_3 \cdot 16WO_3 \cdot 4H_2O$
Silver Praseodymium: $4Ag_2O \cdot Pr_2O_3 16WO_3 \cdot 8H_2O$

The Octodecatungstates:
Alumino-arsenotungstates:
$6(NH_4)_2O \cdot 2Al_2O_3 \cdot 3As_2O_5 \cdot 18WO_3 \cdot 14H_2O$
$4BaO \cdot 2Al_2O_3 \cdot 3As_2O_5 \cdot 18WO_3 \cdot 12H_2O$
$4CdO \cdot 2Al_2O_3 \cdot 3As_2O_5 \cdot 18WO_3 \cdot 17H_2O$
Alumino-antimoniotungstates:
$6(NH_4)_2O \cdot 2Al_2O_3 \cdot Sb_2O_5 \cdot 18WO_3 \cdot 17H_2O$
$5BaO \cdot 2Al_2O_3 \cdot 3Sb_2O_5 \cdot 18WO_3 \cdot 6H_2O$
$6Ag_2O \cdot 2Al_2O_3 \cdot 3Sb_2O_5 \cdot 18WO_3 \cdot 12H_2O$
Potassium Arsenito: $7K_2O \cdot As_2O_3 18WO_3 \cdot 24H_2O$

The Nonadecatungstates:
Potassium Antimonito: $8K_2O \cdot Sb_2O_3 \cdot 19WO_3 \cdot 37H_2O$

The Docositungstates:
Sodium: $5Na_2O \cdot 12WO_3 \cdot 5Na_2O \cdot 10WO_3 \cdot 51H_2O$
Zinc: $9ZnO \cdot 22WO_3 \cdot 66H_2O$

Some Other Complex Tungstates:
Ammonium Silver Alumino Tungstate:
$11Ag_2O \cdot 21(NH_4)_2O \cdot 4Al_2O_3 \cdot 36WO_3$
Ammonio-Tungstates:
$Ag_2WO_4 \cdot 4NH_3$
$CuWO_4 \cdot 2NH_3 \cdot H_2O$
$CuWO_4 \cdot 4NH_3$
$CuO \cdot 4WO_3 \cdot 6NH_3 \cdot 8H_2O$
$ZnWO_4 \cdot 4NH_3 \cdot 3H_2O$
Barium Ferric Tungstate: $21BaO \cdot 2Fe_2O_3 \cdot 45WO_3 \cdot 27H_2O$
Double Ammonium Sodium Tungstates:
$3(NH_4)_2O \cdot 3Na_2O \cdot 16WO_3 \cdot 22H_2O$
$16(NH_4)_2O \cdot 4Na_2O \cdot 50WO_3 \cdot 50H_2O$
$6(NH_4)_2O \cdot 5Na_2O \cdot 24WO_3 \cdot 27H_2O$

Hydroxylamine Ammonium Tungstate:

$NH_4O \cdot WO_4NH_4$

Potassium Ferric Tungstate:

$9K_2O \cdot 12H_2O \cdot 2Fe_2O_3 \cdot 45WO_3 + 54H_2O$

Tungstate of Hydroxylamine: $4NH_2OH \cdot 3WO_3 \cdot 3H_2O$

The Pertungstates

Sodium Monoperditungstate, $Na_2W_2O_8 \cdot 2H_2O$, is prepared by boiling for a few minutes a solution of sodium paratungstate with hydrogen dioxide until it no longer gives a precipitate with nitric acid. The crystals are soluble in water.

Silver Perditungstate, $Ag_2W_2O_8 \cdot 4H_2O$, is obtained by adding silver nitrate to a solution of potassium pertungstate.

Strontium Perditungstate, $SrW_2O_8 \cdot 6H_2O$, is prepared by adding an excess of strontium citrate to a solution of potassium hypertungstate containing a little hydrogen dioxide.

Barium Perditungstate, $BaW_2O_8 \cdot 6H_2O$, is prepared in a manner similar to that for strontium perditungstate.

Sodium Perditungstate, $Na_2W_2O_9 \cdot 6H_2O$, is prepared by warming for ten minutes a solution of sodium paratungstate with hydrogen dioxide and precipitating the sale by the addition of alcohol. The white powder deliquesces a little in air, and forms hydrogen dioxide with dilute sulfuric acid and ozone with concentrated sulfuric acid.

Sodium Dipertungstate, $Na_2O_2 \cdot WO_4 \cdot H_2O_2$ or $Na_2O_2 \cdot WO_5 \cdot H_2O$, is obtained by adding cooled hydrogen peroxide and aqueous sodium hydroxide solutions to a cooled solution of sodium pertungstate and precipitating the salt with alcohol at −12°. Another compound, $Na_2O_2 \cdot WO_4 \cdot H_2O + (Na_2O_2)_2 \cdot WO_4 + 7H_2O$, behaving chemically like the preceding salt, is obtained in analogous manner. These are stable in air.

The following pertungstates have been described:

Cesium Perdodecatungstate:	$Cs_6W_{12}O_{41} \cdot 12H_2O$
Calcium Perhexatungstate:	$Ca_3W_6O_{27} \cdot 8H_2O$
Cesium Perparatungstate:	$Cs_{10}W_{12}O_{65} \cdot 11H_2O$
Lithium Pertetratungstate:	$Li_6W_4O_{16} \cdot 9H_2O$
Magnesium Pertetratungstate:	$Mg_2W_4O_{20} \cdot 9H_2O$
Potassium Hypertungstate:	$K_2O_4 \cdot WO_4 \cdot H_2O$
Potassium Hyperditungstate:	$K_2WO_2O_{11} \cdot 4H_2O$
Potassium Perdecatungstate:	$K_{14}W_{30}O_{52} \cdot 22H_2O$
Rubidium Pertetratungstate:	$Rb_4W_4O_{15} \cdot 3H_2O$
Rubidium Perparatungstate:	$Rb^{10}W_{12}O_{44} \cdot 12H_2O$

Tungsten Bronzes

As early as 1824 F. Wöhler observed that when acid sodium tungstate is reduced by hydrogen, a bronze-colored powder is obtained. This fact has led to the investigation of the compounds now known as tungsten bronzes which, forming a series, are reduction products of the tungstates of the alkali and alkaline-earth metals. These substances have been designated as tungsten bronzes because, owing to their intense and vivid colors, they can be used as substitutes for bronze powders, which are employed as paints for ornamental and decorative purposes. The exact constitution of tungsten bronzes is not known. They appear to contain several hexavalent tungsten atoms and one tetravalent WO_2. Their composition can be represented by the formula $R_2O \cdot (WO_3)_x \cdot WO_2$ or simply $R_2(WO_3)_{x+1}$"

Tungsten bronzes may be prepared by the following methods:

(1) Reduction of an acid tungstate with hydrogen, coal gas, or tin, zinc or iron at a high temperature.

(2) Electrolytic reduction of a fused tungstate; or of a fused mixture of tungstic acid with a metallic carbonate; or of a solution of tungstic acid in a fused mixture of alkali chlorides.

(3) Synthesis by melting mixtures of normal or acid tungstates with tungsten dioxide, in absence of air.

The color of tungsten bronzes ranges from golden-yellow, reddish-yellow, purple-red, violet, blue to bluish-black. The colors change in the order indicated, according to the proportionate increase of tungsten. These bronzes are usually crystalline, generally as cubes or needles. Their specific gravity ranges from 6.5 to 7.5. They are insoluble in water, and with the exception of hydrofluoric are not attacked by the acids. They are decomposed by fusion with alkali, sulfur, ammonium persulfate, or ammonium hydrogen sulfate. The various tungsten bronzes are reduced to sodium tungstate and tungsten at 650 to 700.

Lithium Tungsten Bronze, $Li_2W_5O_{15}$, is prepared as deep blue microscopic prisms by melting lithium paratungstate with tin, or by electrolysis of fused lithium paratungstate.

Other bronzes of composition $Li_2W_4O_{12}$ and $Li_2W_7O_{21}$ have been prepared.

Lithium Potassium Tungsten Bronze, $Li_2W_5O_{15} \cdot 3K_2W_4O_{12}$, is obtained as violet needles by reducing with tin a fused mixture of equimolar proportions of lithium and potassium tungstates.

Potassium Tungsten Bronze, $K_2W_4O_{12}$, is prepared by melting together potassium carbonate and tungstic acid, according to method (1) or by electrolysis according to method (2). The product obtained is in reddish-violet prisms. A suspension appears blue by transmitted and green by reflected light.

Potassium Sodium Tungsten Bronzes, $5K_2W_4O_{12}\cdot 2Na_4W_5O_{15}$ and $3K_2W_4O_{12}\cdot 2Na_2W_3O_9$, have been prepared by von Knorre by fusing together equimolar proportions of sodium and potassium paratungstates and heating the mixture to redness in hydrogen. The former compound is purple-red and the latter dark-red; the former appears blue when powdered.

Sodium Tungsten Bronzes. The following compounds have been prepared:

$Na_2W_2O_6$, golden-yellow cubic crystals
$Na_2W_3O_9$, reddish-purple octahedra
$Na_2W_4O_{12}$, violet needles
$Na_2W_5O_{15}$, blue cubic crystals
$Na_4W_5O_{15}$, reddish-yellow crystals
$Na_6W_6O_{18}$, yellow cubes

Alkali-alkaline earth tungsten bronzes. E. Engels has described the following bronzes:

$2BaW_4O_{12}\cdot 3Na_2W_5O_{15}$, dark blue crystals.
$BaW_4O_{12}\cdot 5Na_2W_3O_9$, yellow-red cubes.
$BaW_4O_{12}\cdot 5K_2W_4O_{12}$, dark red pyramids.
$SrW_4O_{12}\cdot 5Na_2W_5O_{15}$, brilliant violet pyramids.
$SrW_4O_{12}\cdot 12Na_2W_3O_9$, carmine-red pyramids.
$SrW_4O_{12}\cdot 5K_2W_4O_{12}$, red pyramids.
$CaW_4O_{12}\cdot 5Na_2W_5O_{15}$, violet pyramids.
$CaW_4O_{12}\cdot 10Na_2W_3O_9$, purple cubes or pyramids.
$CaW_4O_{12}\cdot 5K_2W_4O_{12}$, glistening red pyramids.

According to E. Theiss, U. S. Patent, 1,896,022 (1933), a metal body can be plated with tungsten bronzes, thus: A 70 per cent solution of barium metatungstate was heated to 80° with the metal to be plated as the anode. A current density of 100 milliamp per sq. cm was maintained. Immediate formation of a blue coherent bronze coating was obtained.

The Halides

(a) **Tungsten Fluorides and Oxyfluorides.** *Tungsten trifluoride*, WF_3. A. Rosenheim and T. H. Li obtained complex salts of WF_3, namely ammonium tungsten tetrafluoride, $(NH_4)WF_4\cdot H_2O$, and potassium tungsten tetrafluoride, $KWF_4\cdot H_2O$.

Tungsten Hexafluoride, WF_6, is obtained by the following methods:

First, $WCl_6 + 6HF = WF_6 + 6HCl$ in platinum vessels
Second, $WCl_6 + 2AsF_3 = WF_6 + 2AsCl_3$
Third, $WCl_6 + 3SbF_5 = WF_6 + 3SbF_3Cl_2$

The last is the most convenient mode of preparation. Tungsten hexafluoride is a colorless gas at ordinary temperature and is ten times as heavy as air. Water decomposes it with the formation of yellow hydrated tungsten trioxide.

Tungsten Oxyfluorides. Tungsten oxytetrafluoride, WOF_4, can be prepared by the action of anhydrous hydrogen fluoride on the oxychloride $WOCl_4$ and by heating tungsten trioxide with lead fluoride, bismuth fluoride or cryolite. At ordinary temperature the oxytetrafluoride forms small colorless hygroscopic plates.

Tungsten Dioxydifluoride, WO_2F_2. Attempts to prepare this compound by itself were not successful, although complex salts of WO_2F_2 have been prepared. Examples of these complex salts are:

Ammonium trifluodioxytungstate, $NH_4F \cdot WO_2F_2 \cdot H_2O$
Sodium tetrafluodioxytungstate, $2NaF \cdot WO_2F_2$
Potassium trifluodioxytungstate, $KF \cdot WO_2F_2 \cdot H_2O$
Copper tetrafluodioxytungstate, $CuF_2 \cdot WO_2F_2 \cdot 4H_2O$
Zinc tetrafluodioxytungstate, $ZnF_2 \cdot WO_2F_2 \cdot 10H_2O$

(b) **Tungsten Chlorides and Oxychlorides.** *Tungsten Dichloride*, WCl. According to H. E. Roscoe, the dichloride is formed when a bath of molten zinc tungsten tetrachloride is heated in a current of carbon dioxide or by the reduction of tungsten hexachloride in hydrogen. The dichloride so formed is grey in color but is unstable in air. The dichloride can also be obtained when the hexachloride is heated with powdered quartz and aluminum, magnesium, zinc, or lead in a current of nitrogen.

Tungsten Trichloride, WCl_3, ($H_3[W_2Cl_9]$ or $2WCl_3 \cdot 3HCl$). The trichloride exists only as double chlorides of trivalent tungsten which with those of potassium, ammonium, rubidium, cesium and thallium, have been prepared by reduction with tin of a solution of potassium tungstate in concentrated hydrochloric acid. The following salts have been prepared: $Cr(NH_3)_6W_2Cl_9 \cdot 2H_2O$; $Co(NH_3)_6W_2Cl_9 \cdot 6H_2O$; $Cu(NH_3)_4NH_4W_2Cl_9 \cdot H_2O$; $Cd(NH_3)_4NH_4W_2Cl_9$; $Cd(NH_3)_4KW_2Cl_9$.

Tungsten Tetrachloride, WCl_4. By partial reduction of the hexachloride with hydrogen, A. Riche obtained tungsten tetrachloride. The tetrachloride may be more readily formed by distilling a mixture of the pentachloride and the hexachloride, heated by a sulfuric acid bath, in a current of hydrogen or carbon dioxide.

Tungsten Pentachloride, WCl_5. The pentachloride is obtained by distilling in carbon dioxide the lower chlorides, formed by reduction of the hexachloride with hydrogen.

Tungsten Hexachloride, WCl_6. When tungsten is heated to redness in the entire absence of air and of moisture, chlorine combines with it to form the hexachloride; at the same time it is extremely difficult to prevent formation of the volatile oxychloride, $WOCl_4$. Another method of obtaining the hexachloride is to have the crystalline disulfide acted upon by chlorine. The hexachloride melts at 275° and boils at 346°. It is reduced by hydrogen into lower chlorides and into the metal.

Oxychlorides. There are two oxychlorides of tungsten, tungsten dioxydichloride (tungstyl, WO_2Cl_2) and tungsten oxytetrachloride ($WOCl_4$), both of which are volatile below 300°. A mixture of these two oxychlorides is obtained by reaction of chlorine with tungsten dioxide. A mixture of these two oxychlorides is obtained by passing chlorine over a mixture of wolframite ore and carbon heated to about 300°. Processes based upon the production of the oxychlorides have been suggested for the metallurgical treatment of tinny wolframite ore.

A. Riche obtained the dioxydichloride by heating tungsten trioxide in dry chlorine; it is obtained by passing the vapor of carbon tetrachloride over red-hot tungsten trioxide and by heating tungsten hexachloride with oxalic acid. The dioxydichloride is a pale-yellow solid with four-sided plates resembling natural boric acid. It is reduced to metal when heated in a current of hydrogen.

Tungsten oxytetrachloride is obtained by heating the sulfide in chlorine, by heating pentachloride or hexachloride in oxygen, or by heating the pentachloride with oxalic acid. It is ruby-red in color, melts at 210°, and boils at 227.5°. Water decomposes it to form tungstic acid.

(c) **Tungsten Bromides and Oxybromides.** Tungsten is attacked by bromine at red heat. The only tungsten bromides known are tungsten dibromide, WBr_2, tungsten pentabromide, WBr_5, and tungsten hexabromide, WBr_6.

Tungsten Dibromide, WBr_2. When hydrogen is passed over tungsten pentabromide heated in a bath of molten zinc, the bluish-black residue is the dibromide.

Tungsten Pentabromide, WBr_5. By passing a current of bromine vapor, preferably diluted with carbon dioxide, but free from air and moisture, over tungsten at red heat, the pentabromide is obtained. It is dark brown in color, melts at 276°, and boils at 333°. The pentabromide is reduced to the dibromide by hydrogen at 350°, and at higher temperature to the metal (E. Defacqz and H. E. Roscoe), and is decomposed by oxygen into a mixture of oxybromide and tungsten trioxide (E. Defacqz).

Tungsten Hexabromide, WBr_6, is formed by gently warming tungsten in bromine vapor in an atmosphere of nitrogen, but in total absence of air and moisture (H. A. Schaffer and E. F. Smith). The hexabromide forms bluish-black crystalline masses and melts readily.

Tungsten Oxybromides. Two tungsten oxybromides are known: they are the dioxydibromide, WO_2Br_2, and the oxytetrabromide, $WOBr_4$. Both are formed when bromine vapor acts on a heated mixture of tungsten and tungsten dioxide, or when the pentabromide is passed over heated trioxide. The separation of these two oxybromides depends upon the fact that the oxytetrabromide is more volatile than the dioxydibromide. The former gives fusible, dark brown needles, melts at 277°, boils at 327°, and is decomposed by water; the latter forms light-red, infusible crystals, which yield a yellow powder, and is inert to cold water.

(d) **Tungsten Iodides and Oxyiodides.** Tungsten hexaiodide and tungsten oxyiodide have not been prepared.

Tungsten Di-iodide, WI_2, is prepared by passing iodine vapor over tungsten heated to redness, or by passing a current of hydrogen iodide over the hexachloride at 400° to 450°. The compound is brown in color and is insoluble in water, alcohol or carbon disulfide.

Tungsten Tetra-iodide, WI_4, is obtained by the action of an excess of liquid hydrogen iodide on tungsten hexachloride at 100°. It is black in color, is not completely stable in air, and is insoluble in water or ether.

Tungsten and Sulfur

Tungsten Disulfide, WS_2, occurs in nature as the mineral tungstenite. It may be prepared by heating tungsten hexachloride in a current of hydrogen sulfide at 375° to 550°, by melting together pure dry potassium carbonate, flowers of sulfur and tungsten anhydride, or by strongly heating metallic tungsten and sulfur.

It is a soft, lustrous, dark-grey crystalline powder. Its specific gravity is 7.5 at 10°.

The trioxide is formed when the disulfide is heated in air. Hydrogen reduces the disulfide completely at 800 to 900°. With fluorine at ordinary temperatures, the fluoride is formed. Chlorine at 400° yields the hexachloride. The disulfide is attacked by bromine at 700°. It is insoluble in water. A mixture of nitric acid and hydrofluoric acid attacks it readily.

Tungsten Trisulfide, WS_3, may be obtained by treating a solution of an alkali thiotungstate with excess of acid.

It is a brown powder which becomes black when dried. The disulfide is formed when the trisulfide is heated in absence of air. When heated in the air, the trisulfide changes to the trioxide. It may be reduced by lime to the metal in an electric furnace. It is slightly soluble in cold water, but more readily in hot water, forming a colloidal solution. It easily dissolves in alkali hydroxides, carbonates and sulfides, forming thiotungstates and colloidal tungsten trisulfide.

Tungsten Sulfochloride, $3WS_3 \cdot WCl_6$, has been prepared by Defacqz by heating a mixture of the hexachloride and liquid hydrogen sulfide in a sealed tube for 36 hours at 60 to 65°. It is a brown powder and is decomposed by water. Nitric acid or fused potash readily oxidizes it.

The Thiotungstates. If the oxygen in tungstates is replaced by sulfur, types of sulfur-containing compounds, or thiotungstates, are obtained₃ They have the following general formulas: R_2WO_3S, $R_2WO_2S_2$, R_2WOS., R_2WO_4. They are formed by dissolving the hydrate of tungstic acid in an alkali hydrosulfide, by the action of hydrogen sulfide on solutions of alkali or neutral tungstates, or by fusing a tungstate with sulfur. The crystals thus obtained are generally yellow to yellowish brown in color, and are soluble in water. The following compounds have been described:

Potassium Monothiotungstate, $K_2WO_3S \cdot H_2O$
Ammonium Dithiotungstate, $(NH_4)_2WO_2S_2$
Potassium Dithiotungstate, $K_2WO_2S_2$
Potassium Trithiotungstate, $K_2WOS_3 \cdot H_2O$
Normal Ammonium Thiotungstate, $(NH_4)_2WS_4$
Normal Potassium Thiotungstate, K_2WS_4
Normal Sodium Thiotungstate, Na_2WS_4
Thiotungstates of Calcium, Strontium and Barium.

Tungsten and Selenium

Tungsten Diselenide, WSe_2, is formed by heating the triselenide.

Tungsten Triselenide, WSe_3, is obtained when acids are added to a solution of sodium acid tungstate, through which hydrogen selenide has already been passed.

Tungsten and Tellurium

Tellurotungstic acid of composition $(CN_3H_6)_6[Te(WO_4)_6] \cdot 3H_2O$ has been described.

Tungsten and Nitrogen

Tungsten nitride is formed if the oxide of tungsten is heated under pressure in a mixture of hydrogen and nitrogen.

Tungsten Dinitride, WN_2, is a clear brown powder, which is decomposed by water, forming ammonia and probably WO_3.

Tungsten Sesquinitride, W_2N_3, may be obtained as a black powder by the action of dry ammonia on tungsten hexachloride. The nitride is oxidized by aqua regia to tungstic acid. When heated in the air it is changed into tungstic acid.

Many nitrides have been described, but the literature concerning them is somewhat contradictory. Other complex nitrides have the following formulas: $4WN_2 \cdot W_2(NH_2)_2 \cdot 2WO_2$, $2WN \cdot W(NH_2)_2$, and $2WN_2 \cdot W(NH_2)_2$

Tungsten and Phosphorus

Tungsten Diphosphide, WP_2, is prepared by washing with carbon disulfide the product obtained by heating tungsten hexachloride at 450° to 500° in a current of dry hydrogen phosphide. The diphosphide, being in black crystals, is insoluble in water but decomposes on fusion. It is acted upon by the halogens on heating, and is reduced to tungsten by copper, zinc, or iron at 1000°. A mixture of either hydrofluoric or hydrochloric acid with nitric acid dissolves it readily.

Tritungsten Tetraphosphide, W_3P_4, is obtained by passing phosphorus vapor over metallic tungsten heated to redness. The grey powder is stable in air.

Tungsten Monophosphide, WP, is prepared by heating a mixture of the diphosphide (1 part) and copper phosphide (20 to 30 parts) at 1200° for three or four hours in the absence of air; the product is then treated with dilute nitric acid. The monophosphide behaves in the same manner as the diphosphide toward oxygen, the halogens and the acids.

Tungsten Subphosphide, W_4P_2, is obtained by heating phosphoric acid with tungstic anhydride in a carbon crucible. It is not attacked by acids but dissolves in a fused mixture of alkali carbonate and nitrate.

Heteropolyacids of Tungsten and Phosphorus. Tungsten and phosphorus jointly form a series of complex acids, the existence of which in the proportions of $P_2O_5:WO_3 = 1:24$, $1:21$, $1:20$, $1:18$ has been established. The following heteropolyacids of tungsten and phosphorus have been described:

12-Tungstophosphoric Acid, $H_7[P(W_2O_7)_6]\cdot xH_2O$, ($P_2O_5:WO_3 = 1:24$). The salts obtained correspond to the general formula $3R_2O\cdot P_2O_5\cdot 24WO_3\cdot xH_2O$. The following salts are known: $2BaO\cdot P_2O_5\cdot 24WO_3\cdot 59H_2O$, $BaO\cdot P_2O_5\cdot 24WO_3\cdot 50H_2O$, and $Ag_2O\cdot P_2O_5\cdot 24WO_3\cdot 60H_2O$.

21:2-Tungstophosphoric Acid, $3H_2O\cdot P_2O_5\cdot 21WO_3\cdot 55H_2O$, ($P_2O_5:WO_3 = 1:21$). The potassium salt is $3K_2O\cdot P_2O_5\cdot 21WO_3\cdot 31H_2O$.

10-Tungstophosphoric Acid ($P_2O_5:WO_3 = 1:20$).

9-Tungstophosphoric Acid, $P_2O_5\cdot 18WO_3\cdot 42H_2O$, ($P_2O_5:WO_3 = 1:18$). The salts of this acid are: $3K_2O\cdot P_2O_5\cdot 18WO_3\cdot 14H_2O$; $3(NH_4)_2O\cdot P_2O_5\cdot 18WO_3\cdot 14H_2O$; $5Ag_2O\cdot P_2O_5\cdot 18WO_3\cdot 34H_2O$; $5(CN_3H_6)_2O\cdot 18WO_3\cdot 18H_2O$.

11-Tungstophosphates ($P_2O_5:WO_3 = 1:22$). The free acid corresponding to this series of salts has not been isolated: $7BaO\cdot P_2O_5\cdot 22WO_3\cdot 54H_2O$; $7K_2O\cdot P_2O_5\cdot 22WO_3\cdot 3H_2O$; $7Na_2O\cdot P_2O_5\cdot 22WO_3\cdot 33H_2O$.

17:2-Tungstophosphates ($P_2O_5:WO_3 = 1:17$): $5K_2O\cdot P_2O_5\cdot 17WO_3\cdot 22H_2O$; $5(NH_4)_2O\cdot P_2O_5\cdot 17WO_3\cdot 16H_2O$; $5Ag_2O\cdot P_2O_5\cdot 17WO_2\cdot 20H_2O$.

3-Tungstophosphates ($P_2O_5:WO_3 = 1:16$): $3K_2O\cdot 3H_2O\cdot P_2O_5\cdot 6WO_3 + 11H_2O$; $3(NH_4)_2O\cdot 3H_2O\cdot P_2O_5\cdot 6WO_3 + 6H_2O$.

Tungsten and Arsenic

Tungsten Diarsenide, WAs_2, is obtained by heating tungsten hexachloride in a current of hydrogen arsenide at a temperature of 150 to 200° for some time and then gradually raising the temperature to 350°. The resulting black crystalline mass is stable in air at ordinary temperature, but is readily oxidized at red heat to yellow tungstic anhydride. The diarsenide is insoluble in water; it is not attacked by solutions of hydrofluoric and hydrochloric acids, but nitric acid and aqua regia oxidize it on warming. It readily combined with chlorine, sulfur and phosphorus when heated. Fused alkalies and alkali carbonates act upon it to form arsenate and tungstate.

Tungsten Chloro-arsenide, W_2AsCl_9, is obtained in bluish-black crystals, by heating tungsten hexachloride with liquid hydrogen arsenide in a sealed tube at 60 to 75°. It is readily decomposed by water, acids and alkalies.

Arsenotungstic Acids and Arsenotungstates are analogous to the phosphotungstic acids and their salts. The investigation of these compounds is as yet very incomplete. Some of the important acids and salts are:

12-Tungsto-arsenates, $(NH_4)_3H_4[As(W_2O_7)_6]\cdot 4H_2O$

11-Tungsto-arsenates, $7BaO\cdot As_2O_5\cdot 22WO_3\cdot 54H_2O$ or $Ba_7[As(OH)(W_2O_7)_5]\text{-}W_2O_7\text{-}[(W_2O_7)_5(OH)As]\cdot 53H_2O$

9-Tungsto-arsenic Acid, (luteo-arsenotungstic acid) $H_5[As(OH)(W_2O_7)_4\text{-}W_2O_7\text{-}(W_2O_7)_4(OH)As]\cdot 36H_2O$

17:2-Tungsto-arsenates, $5(NH_4)_2O\cdot As2O_5\cdot 17WO_3\cdot 16H_2O$ and $5K_2O.As_2O_5\cdot 17WO_3\cdot 22H_2O$

Tungsto-arsenites. The following compounds may be obtained by treating solutions of tungstates with arsenious acid:

$7(NH_4)_2O\cdot 2As_2O_3\cdot 18WO_3\cdot 18H_2O$
$4BaO\cdot As_2O_3\cdot 9WO_3\cdot 21H_2O$
$9Na_2O\cdot 8As_2O_3\cdot 16WO_3\cdot 55H_2O$
$10K_2O\cdot As_2O_3\cdot 4As_2O_5\cdot 21WO_3\cdot 26H_2O$
$10K_2O\cdot 14As_2O_3\cdot 3P_2O_5\cdot 32WO_3\cdot 28H_2O$
$5K_2O\cdot Na_2O\cdot 2As_2O_3\cdot 2P_2O_5\cdot 12WO_3\cdot 15H_2O$
$7K_2O\cdot As_2O_3\cdot 4P_2O_5\cdot 60WO_3\cdot 55H_2O$

Tungsten and Antimony

Potassium Antimoniotungstate, $2WO_3\cdot 3KSbO_3\cdot 8H_2O$, is obtained by boiling a solution of potassium paratungstate with excess of antimonic acid.

Other salts have already been mentioned.

Tungsten and Bismuth

There have been described several complex compounds of the type $3R'_2O \cdot 2BiO_3 \cdot 11WO_3 \cdot xH_2O$. The bismuthotungstates of potassium, ammonium and strontium are yellow in color when dried. Mercurous bismuthotungstate, $3Hg_2O \cdot 2Bi_2O_3 \cdot 11WO_3 \cdot 15H_2O$, has been prepared.

Tungsten and Vanadium

The three well-defined series of complex salts containing tungsten and vanadium are:

(1) The dichromate colored series, $5R'_2O \cdot 3V_2O_5 \cdot 6WO_3 \cdot xH_2O$ ($R' =$ NH_4, K, Na).

(2) The yellowish-red salts, $2R'_2O \cdot V_2O_5 \cdot 4WO_3 \cdot xH_2O$. Salts of the alkali metals, alkaline-earth metals and silver have been prepared.

(3) The deep red salts, $5R'_2O \cdot 3V_2O_5 \cdot 14WO_3 \cdot xH_2O$. Salts of ammonium, potassium, cesium, and barium have been prepared.

Three series of silico-vanadotungstates of the following composition have been described: $3R'_2O \cdot SiO_2 \cdot V_2O_5 \cdot 9WO_3 \cdot xH_2O$; $3R'_2O \cdot SiO_2 \cdot V_2O_5 \cdot 10WO_3 \cdot xH_2O$; $7R'_2O \cdot 2SiO_2 \cdot 3V_2O_5 \cdot 18WO_3 \cdot xH_2O$.

Tungsten and Carbon

Compounds containing these two elements are discussed in Chapter IV on Metallurgy.

Tungsten Carbonyl. Tungsten carbonyl can be produced first by reducing tungsten acid with hydrogen at 800° in the presence of copper nitrate (equivalent to 10 per cent copper in the reduced material) and then converting to the carbonyl with carbon monoxide, at 200 atmosphere and 275 to 300°. Arsenic, phosphorus or sulfur or their compounds are added to prevent undesirable decomposition of the carbon monoxide. The carbonyls are removed by cooling or by washing out with ether or benzene (U. S. Patents 1,894,239 and 1,921,536 and French Patent 708,260).

Tungsten and Cyanogen

Only two well-defined series of complex cyanides are known. They are:

(1) $R'_4[W(CN)_8]$, containing tetravalent tungsten;

(2) $R'_3[W(CN)_8]$, containing pentavalent tungsten.

Tungstocyanic Acid, $H_4[W(CN)_8] \cdot 6H_2O$, may be prepared by saturating with hydrogen chloride below 0° the clear filtrate, obtained from treatment of silver salt in the presence of a slight excess of cold dilute hydrochloric acid. The product is soluble in water and alcohol. As it is a strong acid, it readily decomposes carbonates. The following salts have been described:

Ammonium Tungstocyanide, $(NH_4)_4[W(CN)_8]$
Calcium Tungstocyanide, $Ca_2[W(CN)_8] \cdot 8H_2O$
Cadmium Tungstocyanide, $Cd_2[W(CN)_8] \cdot 8H_2O$
Cesium Tungstocyanide, $Cs_4[W(CN)_8]$
Lead Tungstocyanide, $Pb_2[W(CN)_8] \cdot 4H_2O$
Magnesium Tungstocyanide, $Mg_2[W(CN)_8] \cdot 6H_2O$
Manganese Tungstocyanide, $Mn_2[W(CN)_8] \cdot 8H_2O$
Potassium Tungstocyanide, $K_4[W(CN)_8] \cdot 2H_2O$
Rubidium Tungstocyanide, $Rb_4[W(CN)_8] \cdot 3H_2O$
Silver Tungstocyanide, $Ag_4[W(CN)_8] \cdot 3H_2O$
Sodium Tungstocyanide, $2Na_4[W(CN)_8] \cdot 5H_2O$
Strontium Tungstocyanide, $Sr_2[W(CN)_8] \cdot 8$ or $9H_2O$
Thallium Tungstocyanide, $Tl_4[W(CN)_8]$
Zinc Tungstocyanide, $Zn_2[W(CN)_8] \cdot 4H_2O$

Tungstocyanic Acid, $H_3[W(CN)_8] \cdot 6H_2O$, is obtained from its silver salt by the action of hydrochloric acid. It is unstable, and decomposes in daylight and in moist air.

The following salts have been described:

$2K_3[W(CN)_8] \cdot 5H_2O$
$Na_3[W(CN)_8] \cdot 4H_2O$
$Rb_3[W(CN)_8] \cdot 2H_2O$
$Cs_3[W(CN)_8] \cdot 2H_2O$
$Ba_3[W(CN)_8]_2 \cdot 10H_2O$
$Sr_3[W(CN)_8]_2 \cdot 11H_2O$

Tungsten and Silicon

Tungsten Sesquisilicide, W_3Si_3, is obtained by fusing in an electric furnace a mixture of 10 parts of silicon and 23 parts of tungstic anhydride. The product is then treated in hydrochloric acid and the excess of free tungsten is removed by electrolysis; the silicide is finally purified with aqua regia, ammonia, hydrofluoric acid and methylene iodide. It is attacked by the halogens at comparatively low temperatures. It is very resistant to acids and alkalies in solution; a mixture of nitric acid and hydrofluoric acids decomposes it at ordinary temperatures; and fused alkali hydroxides and carbonates readily attack it.

Tungsten Disilicide, WSi_2, is obtained by fusing a mixture of copper silicide and amorphous tungsten in an electric furnace. The product is washed and treated successively with nitric acid, sodium hydroxide, warm hydrofluoric acid and water. When heated slightly, the disilicide is attacked by fluorine. Chlorine attacks it at 450°, yielding silicon tetrachloride and tungsten hexachloride. A mixture of nitric and hydrofluoric acids or fused alkalies decomposes it.

Tungsten Trisilicide, WSi_3, may be obtained by successfully treating a mixed iron silicide, containing 9 per cent iron, 51.6 per cent tungsten and

38.4 per cent silicon, with concentrated hydrofluoric acid, hot concentrated sodium hydroxide, and dilute hydrofluoric acid. The trisilicide exhibits chemical properties similar to those of the disilicide.

The following tungstosilicic acids and tungstosilicates have been described:

12-Tungstosilicic Acid, $H_8[Si(W_2O_7)_6] \cdot xH_2O$
Potassium salt: $K_8[Si(W_2O_7)_6] \cdot 14H_2O$
Mercurous salt: $Hg_8[Si(W_2O_7)_6] \cdot 5H_2O$
Sodium salt: $Na_4H_4[Si(W_2O_7)_6] \cdot 18H_2O$
Lithium salt: $Li_4H_4[Si(W_2O_7)_6] \cdot 22H_2O$
Calcium salt: $Ca_2H_4[Si(W_2O_7)_6] \cdot 22H_2O$
Barium salt: $Ba_2H_4[Si(W_2O_7)_6] \cdot 22H_2O$
Iso-12-Tungstosilicic Acid, $H_8[Si(W_2O_7)_6] \cdot 20H_2O$
$Na_4H_4[Si(W_2O_7)_6] \cdot 10H_2O$
$(NH_4)_4H_4[Si(W_2O_7)_6] \cdot 6H_2O$
$K^8[Si(W_2O_7)_6] \cdot 20H_2O$
$(NH_4)_8[Si(W_2O_7)_6] \cdot 16H_2O$
10-Tungstosilicates, $(NH_4)_8[SiO(W_2O_7)_5] \cdot 8H_2O$
$K_7[Si(OH)\ (W_2O_7)_5] \cdot 11H_2O$

Tungsten and Boron

Tungsten Boride, WB_2, is prepared by heating a mixture containing 4 grams of tungsten and 0.2 gram of boron in an electric furnace. The crystals thus obtained are octahedral and are silvery and metallic on fracture. Concentrated acids attack the boride. Chlorine decomposes it at 100°. It readily dissolves in a fused mixture of sodium carbonate and potassium nitrate.

12-Tungstoboric Acid, $H_9[B(W_2O_7)_6] \cdot 28H_2O$, and *Iso-12-Tungstoboric Acid*, $H_9[B(W_2O_7)_6] \cdot 22H_2O$ are prepared thus: Add sufficient water to a mixture consisting of 1 part of normal sodium tungstate and 1.5 parts of boric acid until a clear solution is formed on boiling. After a time a mixture of sodium borate and boric acid separates. After filtering, the mother liquor is treated with more boric acid and the procedure is repeated. The solution is then treated with sulfuric acid and ether. After the resulting product is decomposed by cold water, it is evaporated in a vacuum, when crystals of two isomeric acids—12-tungstoboric acid and iso-12-tungstoboric acid—separate out.

A well-defined series of salts of composition $R_5H_4[B(W_2O_7)_6] \cdot xH_2O$ (R = NH_4, Li, K, Na, Ag; R_2 = Ba, Ca, Cd, Cu, Mg, N) has been obtained by adding metal hydroxide or carbonate to 12-tungstoboric acid.

References

1. Friend, J. Newton, "A Text-Book of Inorganic Chemistry," Vol. VII, Part III: Vallance, Reece H., and Eldridge, Arthur A.: "Chromium and its Congeners," Chapter 6, Tungsten, pp. 181-271 (Charles, Griffin & Co.), London, 1926.
2. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, pp. 673-874 (Longmans, Green & Co.), 1931.
3. "Gmelin's Handbuch der anorganischen Chemie," 8 Auflage, System-Number 54: Wolfram; herausgegeben von der Deutschen Chemischen Gesellschaft, Verlag Chemie, Berlin, 1933.

Chapter VI

Analysis of Tungsten

DETECTION

1. When an ore of tungsten is heated with aqua regia, lemon-yellow tungstic acid is obtained. When tungstic acid is treated with hydrochloric acid and zinc, aluminum or tin it turns a beautiful blue color because of its reduction to the pentoxide, $W_2O_5 \cdot xWO_3$.

2. To detect the presence of tungsten in ores in very minute amounts, mix the pulverized ore with several times its volume of sodium carbonate, add a little water to make a paste, and fuse in a loop of platinum wire. Pulverize the bead and dissolve in a little water. The presence of tungsten in the solution may be detected by the following sensitive tests:

A. On spot-test paper add one drop of concentrated hydrochloric acid, one drop of the solution in the center of the moist area, one drop of $2N$ potassium thiocyanate solution and one drop of normal stannous chloride in concentrated hydrochloric acid. When tungsten is present the middle of the moist spot turns greenish blue.[1]

B. To a drop of the solution in a micro-test tube add a drop of diphenyline hydrochloride. The presence of tungsten is indicated by precipitation or cloudiness in the tube.[2]

3. The salt of phosphorus bead of tungsten is colorless in an oxidizing flame, and blue in a reducing flame, becoming blood-red on addition of $FeSO_4$.[3]

QUANTITATIVE ANALYSIS

The general practice for the quantitative determination of tungsten is gravimetric, the tungsten being weighed as its trioxide. This trioxide is best obtained by igniting tungstic acid precipitated in slightly acid solution with cinchonine chloride. Other methods include the precipitation of tungstic acid by mercurous nitrate and by many other organic reagents such as benzidine,[10] rhodamine B, tannic acid and antipyrine, anti-1,5-di-(*p*-methoxyphenyl)-1 hydroxylamino-3 oximino-4-pentene[11], all of which yield the trioxide on ignition.

On separating tungsten from the other components in the ore some silica tends to follow tungsten, and vice versa, when the amount of silica present is large. For this reason, when tungsten is determined in highly siliceous ores, the hydrofluoric acid method for tungsten metal is preferred.

DETERMINATION IN ORES

Cinchonine Method[4]

The following procedure for tungsten concentrates requires approximately three 8-hour days. It is shorter and less accurate than most standard procedures, but suffices for all practical purposes.

Procedure. Grind the ore in an agate mortar to finer than 300 mesh. Weigh a 1-gram sample and place it in a 400-ml beaker. Add 5 ml of water and swerve to spread the sample evenly over the bottom of the beaker. Add 100 ml of hydrochloric acid, cover the beaker and heat for 1 hour at just below boiling. Remove the cover, break up any cake on the bottom of the beaker with a stirring rod and evaporate to a volume of about 40 ml. Scrape the bottom of the beaker again to break up any crust and add 40 ml of hydrochloric acid and 15 ml of nitric acid. Replace the cover and heat gently until all danger of spattering is over, then remove the cover and evaporate down to about 15 ml. Add 125 ml of hot water and heat slowly to boiling. The above should require approximately 8 hours and is most satisfactorily carried out without interruption. Allow the sample to stand for several hours, or preferably overnight.

Filter the solution through an 11-ml filter paper covered with some ashless filter-paper pulp. Wash the precipitate from the beaker into the filter with a jet from a wash bottle containing a 10 per cent solution of hydrochloric acid. Wash the beaker (twice) and the filter (6 times) thoroughly with the same 10 per cent acid solution, add 2 cc of cinchonine solution, stir the filtrate vigorously and set aside for possible recovery of tungstic acid (Precipitate 1). Wash the residue on the filter back into the original beaker with a jet of hot water from a wash bottle and save the filter. It is preferable to leave a little residue on the filter rather than to use more than 25 ml of water for this transfer. Add 5 ml of ammonium hydroxide, cover the beaker and heat gently until all the yellow tungstic acid is dissolved. Filter this solution through the filter used before, receiving the filtrate in a 400-ml beaker. Wash the beaker (3 times) and filter (4 times) with a 10 per cent solution of ammonium hydroxide. All undissolved mineral particles in the beaker must be transferred onto the filter. If necessary, this may be accomplished by wiping the beaker with a small piece of filter paper; then crumple the paper and place it on the filter. Reserve the residue (Residue 1). To the filtrate add 200 ml of hot water, then boil gently to expel all traces of ammonia. Dilute to 300 ml with hot water, add 2 ml of hydrochloric acid with stirring and 8 ml of cinchonine solution with vigorous stirring to coagulate the precipitate (Precipitate 2).

Ignite Residue 1 in a 30-ml nickel crucible. Mix the ash with 5 to 6 times its volume of sodium carbonate and fuse over the full flame of a Meker-type burner. After cooling, place the crucible on its side in a 250-ml beaker. Add enough hot water to cover the crucible and heat gently to dissolve the fused mass. Filter the solution and receive the filtrate in a 400-ml beaker. Wash the crucible, beaker and filter with hot water. To the filtrate slowly add 10 ml of hydrochloric acid with stirring. Cover the beaker and boil to expel all carbon dioxide. Add hot water to make the volume up to 300 ml and add 4 ml of cinchonine solution with vigorous stirring. (Precipitate 3). The above should constitute the second day of work. Allow the precipitates to stand overnight.

Filter Precipitates 1, 2 (if any is visible) and 3 on a 12.5-cm ashless filter paper covered with some ashless filter-paper pulp. Wash the beakers (twice) and filter (3 times) with cinchonine wash solution after each beaker is emptied. If any precipitate remains on the side of the beaker, wipe it off with a small piece of ashless filter paper and add the paper to the precipitate on the filter. Finally wash the filter with a little water. Transfer the filter paper and the precipitate into a previously ignited and weighed 50-ml platinum evaporating dish. Slowly char the paper; then ignite in a muffle furnace to constant weight. Increase the temperature in the furnace gradually to 750°. Cool the residue. Add 1 drop of sulfuric acid and enough hydrofluoric acid to moisten the impure tungstic acid and evaporate to dryness. Heat gradually to red heat to expel sulfuric acid. Cool in a desiccator and weigh to obtain the weight of tungstic oxide.

The tungstic oxide thus obtained should be bright lemon-yellow. Occasionally it is visibly contaminated with iron. To correct the weight of this oxide, fuse it with sodium carbonate as in the treatment of Residue 1, except in this case filter on ashless filter paper, ignite the residue and fuse again. Again filter on ashless paper and ignite the residue. Subtract the weight of any oxide obtained from the weight of the tungstic acid.

Separation of Tantalum and Columbium

In the assay of ore for tungstic oxide it is often required to make a separation of tantalum and columbium from the ignited oxide.

Procedure[5]. After having weighed the oxide dissolve it in the platinum dish with 2 grams of sodium hydroxide and 10 ml of water on a steam bath. Transfer the contents of the platinum dish to a small beaker, dilute to 100 ml and add tartaric acid until the solution is acid to litmus. Then add 5 grams of excess tartaric acid. Cool to room temperature, add some filter-paper pulp and add 10–15 ml of 6 per cent cupferron solution slowly with stirring. Filter on ashless paper, preferably on a cone and with suction. Wash the filter residue with cold 1 per cent tartaric acid solution and ignite at low temperature. Dissolve the ignition residue in several ml of hydrofluoric acid and evaporate almost to dryness on a steam bath. Add 10 ml of 20 per cent tartaric acid, and 5 ml of 4 per cent boric acid; then dilute to 100 ml and precipitate again with cupferron. Filter the precipitate as before and wash with 10 per cent hydrochloric acid. Ignite in the same platinum dish and weigh. Subtract the weight of the residue from the weight of tungstic oxide previously obtained.

Cupferron precipitates all of the Ta, Cb, Zr, Ti and Fe that may be present, but not W or Mo. It is good practice to test the filtrate for Mo, although it is rarely present.

Brief Method

This simplified procedure can be carried out in several hours and gives a consistently low evaluation of tungstic oxide because of the incomplete precipitation of tungstic acid from a solution containing alkaline salts.

Procedure. Mix a 1-gram sample in a 30-ml nickel or iron crucible with 6 to 8 grams of sodium peroxide, spread a thin layer of sodium peroxide on top and fuse over a Meker-type burner. When cooled, place the crucible on its side in a 400-ml beaker, cover the beaker and add 40 ml of concentrated hydrochloric acid. Without removing the cover, add water a little at a time by means of a wash bottle until no more reaction is observable after an addition of water. Remove the crucible, wash it thoroughly both inside and outside with hot dilute hydrochloric acid. Bring the volume of solution in the beaker up to 300 ml, add 5 ml of cinchonine solution and boil for several minutes. Allow the solution to cool and stand longer if possible. Filter over ashless filter paper, wash the filter and precipitate 3 times with cinchonine wash solution. Ignite the precipitate, treat it with hydrofluoric acid, and weigh as tungsten trioxide, as in the assay procedure.

Rhodamine B Method[12]

Weight the required amount of finely powdered sample and place in a 250 ml beaker. Moisten, add 50 ml hydrochloric acid, cover and heat at low temperature for one half hour with occasional stirring. Then evaporate down to 25 ml, add 10 ml of nitric acid and again evaporate to 8 ml. Add 100 ml of boiling water, stir and boil gently for a few minutes; then add rhodamine B reagent, stirring vigorously. Again boil to coagulate the precipitate. Allow the beaker to stand for a half hour. Filter and wash twice with hot rhodamine B wash solution, followed by a hot 2 per cent hydrochloric acid solution. Transfer the filter paper to the original beaker and add 20 ml of water and 7 ml of ammonium hydroxide. Macerate the filter paper and rinse the sides of the beaker with warm dilute ammonia wash solution. Cover, warm gently with occasional stirring for about 10 minutes. Filter into a 250 ml beaker, wash well with warm ammonia wash solution. The total volume is about 200 ml. Evaporate down to 100 ml and add the required amount of rhodamine B reagent. Stir well while adding concentrated hydrochloric acid, dropwise, until precipitation is permanent, then add two drops in excess. Add filter paper pulp, stir vigorously and bring to a boil. Allow precipitate to settle for a few minutes and filter through ashless filter paper, washing with hot rhodamine B solution. Transfer the filter with the precipitate to a weighed platinum dish and continue as in the cinchonine method.

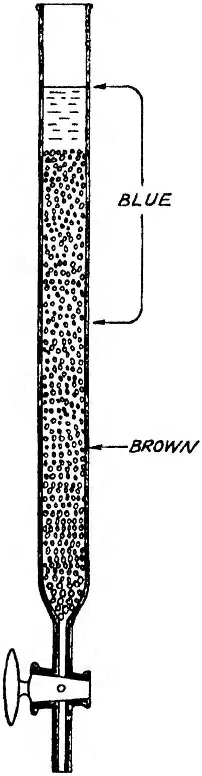
Tannic Acid-antipyrine Method for Low-grade Ores[13]

Weigh the required amount of sample and place in a 250 ml beaker, add 50 ml of hydrochloric acid, cover and digest for about 3 hours at a low temperature. Then add 20 ml more hydrochloric acid and 20 ml of nitric acid and evaporate down to 10 ml. Add 15 ml of perchloric acid and take to strong fumes. Cool, add 5 ml of hydrochloric acid and 200 ml hot water, boil and filter; wash the paper (six times) with hot 5 per cent hydrochloric solution. Discard the filtrate and wash the residue back into the original beaker. Add 10 ml ammonium hydroxide and several grams of ammonium chloride. Boil 5 minutes and filter through the same paper. Wash the beaker and paper with a hot ammonia wash solution, and discard the residue. Boil the filtrate to expel the free ammonia. Dilute to 200 ml with hot water and acidify with sulfuric acid adding 6 ml in excess. Add 8 grams of ammonium sulfate and bring to a boil. Then add 5 ml of 10 per cent tannic acid solution and a little ashless paper pulp. Cool to room temperature and add 10 ml of 10 per cent antipyrine solution, stirring vigorously. (Add 5 ml of tannic acid and 10 ml of antipyrine solution for every 100 mg of tungstic oxide.) Filter the solution and wash with a cold antipyrine-sulfuric acid wash solution. Wipe the beaker with a small piece of ashless filter paper and add the paper to the precipitate. Transfer the filter paper with the precipitate to a weighed platinum dish and continue as in the cinchonine method.

Volumetric Method

The following procedure, requiring less than 4 hours, is highly satisfactory for routine estimation. When used on high-grade concentrates its deviation from gravimetric determination is about 0.5 per cent. It is based on the reduction of WO_3 to WO_2 with zinc and reoxidizing to WO_3 with potassium permanganate.

Procedure. Fuse 0.5 to 1 gram of the finely powdered sample with 5 grams of $NaKCO_3$ in a porcelain or platinum crucible for 30 minutes. Dissolve the fused mass in a minimum of hot water. Filter the solution and wash with hot water. Acidify the filtrate with concentrated sulfuric acid, using 5 ml excess. Heat the solution to 80-90° and pass it through a Jones Reductor at such a rate that only a brown colloidal precipitate of WO_2 emerges through the zinc column. Wash the zinc column free of all brown residue with 150 ml of 3 N H_2SO_4 and finish washing with some water. Titrate the solution at 50 to 60° with 0.1 N $KMnO_4$ to a pink tinge.



Jones reductor for volumetric analysis of tungsten.

The solution passing through the reductor should not exceed 100 ml in volume. The amount of $KMnO_4$ used in each titration should not exceed 50 ml. If the WO_3 content is very high, dilute the alkaline filtrate, divide it into two parts and treat separately.

Colorimetric Method for Low Grade Ores and Tailings[14]

A. *General Method:*

Weigh one gram of finely ground sample in an iron crucible and fuse with five grams of sodium peroxide. Cool the fused mass and digest with hot water containing a little alcohol. Filter into a 250 ml volumetric flask and wash with a warm 0.5 per cent solution of sodium hydroxide. Use a 10 ml aliquot in a 50 ml beaker, to which add 0.5 ml of water, 1 ml of potassium thiocyanate solution, 5 ml of stannous chloride solution and 10 ml of concentrated hydrochloric acid in the order mentioned. At the same time prepare a standard containing 0.20 mg of WO_3 in the following manner: Into a 50 ml beaker pipette 5 ml of standard sodium tungstate solution (1 ml-0.0004 gram of WO_3), 5 ml of water, 0.5 ml of sodium hydroxide (approximately 20 per cent). Then add the reagents mentioned above. After one and a half hours compare the sample against the standard in a colorimeter.

B. *Preferred Method—When Molybdenite or Arsenic Is Present:*

Weigh 0.5 to 2 grams of finely ground sample in a 100 ml beaker, add 1 ml of 1 to 3 phosphoric acid and 04 ml of concentrated hydrochloric acid. Digest the solution on the steam bath for 20 minutes and then evaporate to dryness. Add 10 ml of 1:4 hydrochloric acid and digest for 10 minutes or more. Dilute to 50 ml with water, warm and add paper pulp. Filter into a 100 ml volumetric flask, wash with water. To a 10 ml aliquot add 0.5 ml of sodium hydroxide (approximately 40 per cent) and 1 ml of potassium thiocyanate solution. Add the stannous chloride and hydrochloric acid as in procedure A. Let the mixture stand for one and a half hours and compare with a standard made at the same time in the manner described in procedure A.

Determination in Metals[4]

Weigh 1 gram of the finely divided metal and place in a 50-ml platinum evaporating dish. Add enough hydrofluoric acid to cover the sample; then add nitric acid, a drop at a time, until no more reaction is observable after a fresh addition. Add 5 ml. of sulfuric acid and evaporate until dense white fumes appear. Wash the contents of the dish into a 250-ml beaker, add 150 ml of water, 10 ml of hydrochloric acid and boil. After cooling, filter on ashless filter paper and wash all the precipitate onto the filter, and wash with a 10 per cent solution of hydrochloric acid. Ignite the filter in the platinum dish and weigh. Fuse the ash in the same dish with 2 or 3 times its volume of sodium carbonate, dissolve the fused mass in water and filter. Ignite the filter in the platinum dish and fuse the ash again with sodium carbonate. Dissolve the fused mass, filter on ashless filter paper, and wash thoroughly with hot water. Finally, ignite the filter again in the platinum dish and weigh. The difference in weight of the igniting residues before and after the two fusions is the weight of tungstic oxide. Multiply this weight by 0.7931 to obtain the weight of tungsten metal in the sample.

Analysis of Tungsten Bronzes[5]

Tungsten compounds usually decompose to yield tungstic acid on boiling with acids. Tungsten bronzes, however, do not decompose very readily in acid, because of difficulty in oxidizing tungsten dioxide to the trioxide. The following is a method of transforming the bronzes to normal tungstates without affecting the alkalies, so that the alkalies can be determined in the same sample.

Procedure. To 0.5 gram of finely powdered bronze in a porcelain crucible add 2 grams of alkali-free ammonium sulfate and 2 cc of sulfuric acid. Heat carefully over a small flame, with frequent rotary motion of the crucible, until some thick fumes of sulfuric acid have been evolved. Allow the mass to cool. Add 1 gram of ammonium sulfate, 1 ml of sulfuric acid and heat again until sulfuric acid fumes evolve thickly; then allow to cool. Nearly fill the crucible with water to soften the mass and rinse into a porcelain dish. Add 50 ml of nitric acid and digest on a water bath for 3 or 4 hours. Dilute the contents of the dish with water, filter off the residue of tungstic acid, ignite and weigh. If it is desired to recover the small amount of tungstic acid in the filtrate, evaporate it as far as possible on the water bath, allow to cool, dilute with water, treat with excess ammonium hydroxide, and evaporate again. Add 20 ml of hydrochloric acid, 10 ml of nitric acid, cover the beaker and evaporate slowly to 15 ml. Rinse down the cover and sides of the beaker and dilute to 150 ml with hot water. Add 5 ml of cinchonine solution with vigorous stirring. After standing several hours filter off any precipitate and add it to the first precipitate.

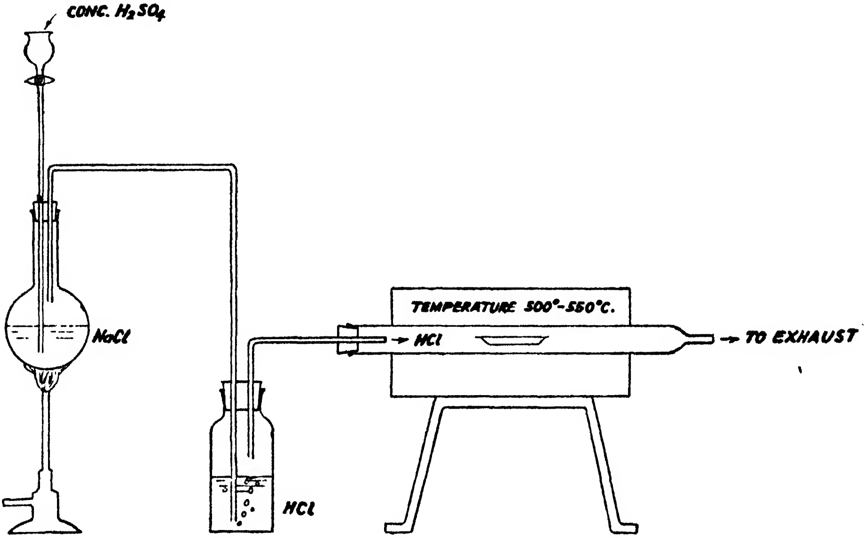
To determine the alkalies, evaporate the final filtrate to dryness, ignite, and weigh the residue as alkali sulfate.

Analysis of Tungsten Powder

The fine tungsten powder is first oxidized to tungstic oxide in a combustion furnace in contact with air or oxygen.

When the oxidation is complete, the tungstic oxide is cooled in a desiccator and a sample of it weighed into a porcelain boat. The boat is then introduced into a combustion furnace and heated to 500–550° in a slow stream of hydrochloric gas. Volatilization of the tungstic oxide is complete when the yellow color of the oxide is no longer evident in the boat. The boat is cooled in a desiccator and the remaining residue weighed as the total non-volatile material.

The non-volatile material is transferred to a beaker and distilled water added. The solution is allowed to stand 2 hours and then filtered through ashless paper, which together with the residue is ignited and weighed. The insoluble residue contains silica, thorium, and other similar impurities; the filtrate, the alkalies. These impurities may be separated and analyzed by the usual methods, wherever required.



Apparatus for analysis of tungsten powder.

The hydrochloric gas can be obtained directly from a hydrochloric gas cylinder, or by the action of sulfuric acid on sodium chloride as shown in the accompanying figure.

Other methods for the volatilization of tungsten can also be used[15], such as, passing air bubbled through chloroform over the sample heated at 600–650°, or chlorine bubbled through sulfurdichloride over the sample heated at 400°.

Determination of Impurities in Tungsten Ore

The following are rapid methods for the estimation of some impurities commonly found in tungsten ores.

Arsenic[6]. Weigh 0.5 to 5 grams of ore into a 500-ml Erlenmeyer flask. Add sufficient water to moisten the ore, 30 ml of concentrated sulfuric acid and 6 ml of phosphorous acid. Fume over a free flame for 10 minutes at such a temperature that no fume is visible within a flask. Cool and add 30 ml of water. Connect to an Allihn condenser plate a 400-ml beaker at the receiving end with just sufficient water to cover the tip of the condenser. Add 25 ml of hydrochloric acid into the flask through a separatory funnel and distill until faint fumes appear in the flask. Disconnect and wash out the condenser with water. Neutralize the solution with sodium hydroxide solution using pH indicator; then make slightly acid with hydrochloric acid. Add excess sodium bicarbonate and titrate with 0.1 *N* iodine solution, using starch indicator.

Phosphorus[7]. Weigh 0.5 to 1 gram of ore into a 250-ml beaker. Moisten it with water, add 50 ml of hydrochloric acid and 15 ml of nitric acid. Digest the sample until the volume of the solution is reduced to 5–10 ml. Add 30 ml of water and boil. Cool for an hour and filter. Wash the precipitate 3 times with a 10 per cent solution of hydrochloric acid. Evaporate the filtrate to dryness but do not bake. Cool, add 15 ml of 70 per cent perchloric acid and fume on a hot plate until the color of the solution changes to straw-yellow. Care must be taken not to over-evaporate the solution. Cool slightly, add 10 ml of ammonium vanadate solution, then boil the solution to drive off chlorine. Filter into a 100-ml volumetric flask, and wash the filter paper 5 times with water. Add 7.5 ml of ammonium molybdate solution and fill the flask to its mark with water. Shake the flask until the precipitation which appears at first is redissolved. Test colorimetrically by Colemann's spectrometer at wave length of 450 millimicrons.

This method is accurate only for scheelite.

Tin. Decompose the sample as in the brief method for the determination of WO_3. When filtering the precipitated WO_3, receive the filtrate in a 500-ml Erlenmeyer flask. Add a coil of metallic nickel and boil for 30 minutes. Into the neck of the flask insert a rubber stopper with a glass tubing through it and then bend it downward outside of the flask. Cool the flask in a tray with the end of the glass tubing immersed in a beaker of sodium bicarbonate solution. When completely cooled, titrate with 0.1 *N* iodine solution, using starch indicator.

Iron. Take the filtrate from the brief WO_3 determination, add 10–20 ml of bromine water and boil. Make the hot solution ammoniacal. Filter the precipitate and wash it with hot water. Dissolve the precipitate with warm hydrochloric acid and wash the filter paper with a 10 per cent solution of the acid. Add test lead to the solution and boil until it is colorless. Titrate immediately with 0.1 *N* potassium dichromate solutions, using potassium ferricyanide as an outside indicator. The end point is reached when the solution and the ferricyanide solution fail to produce blue color for 30 seconds.

Lime. Boil the ammoniacal filtrate from the determination of iron to drive off ammonia. Dilute the solution to 300 ml, add 10 ml of hydrochloric acid and 25 ml of 4½ per cent oxalic acid. Boil the solution and add to the hot solution an excess of 1:1 ammonium hydroxide. Allow to stand at least an hour and filter. Wash the precipitate with hot water. Dissolve the precipitate in dilute sulfuric acid and titrate with standard potassium permanganate solution to a pink tinge.

Antimony[8]. Take the distillation residue from the determination of arsenic, transfer it into a 600-ml beaker, dilute to 500 ml with water and titrate with 0.1 *N* potassium permanganate solution. This rapid method will give an accuracy of well within 0.5 per cent.

Copper. Fuse 1 to 5 grams of sample and dissolve the fused mass as in the determination for tungstic oxide. After filtering off the tungstic oxide, pass hydrogen sulfide through the filtrate. Filter off the precipitate, wash it back into the original beaker and heat it to boiling with 30 ml of KSH solution. Filter the hot solution through the same filter paper and wash with 1 per cent KSH solution. Return the filter paper and residue into the same beaker and heat to fuming with 5 ml of sulfuric acid and 20 ml or more of nitric acid to decompose all organic matter. Dilute the solution and make it ammoniacal. Transfer the solution into a Nessler tube and make it up to volume with 3 *N* ammonium hydroxide. Compare the sample with a standard sample by Coleman's spectrometer at a wave length of 620 millimicrons.

Standard solution: Dissolve electrolytic copper in nitric acid and add to 3 *N* ammonium hydroxide solution.

Sulfur. The combustion method of Kassler[9] commonly used for steel and ferro-alloys may be adopted for very rapid routine determination of sulfur in tungsten ores not containing barium sulfate. Briefly this method calls for heating the sample in a tube furnace at approximately 2400°F under a stream of oxygen. Pass the combustion gases through a dilute solution of ammonium acetate, simultaneously titrating the solution with standard iodine solution, with starch indicator. Keep the iodine solution slightly in excess until close to the end of the titration. This determination requires only several minutes with a hot furnace.

Note: Solutions used in this chapter:

Ammonium Molybdate Solution: Dissolve 50 grams of molybdic acid in 200 ml of water, and 40 ml of concentrated ammonium hydroxide. Filter the solution, boil the filtrate for 20 minutes, then dilute to 500 ml.

Ammonium Vanadate Solution: Dissolve 2.35 grams of ammonium vanadate in 500 ml of hot water. Add 20 ml of 1:1 nitric acid, then dilute to 1 liter.

Chapter VII

The Industrial Application of Tungsten

The yearly consumption of tungsten for various industrial applications in the United States may be roughly distributed as follows:

Ferrous alloys	90.00 per cent
Tungsten carbide	5.0 " "
Stellite	2.0 " "
Electrical equipment	1.5 " "
Miscellaneous	1.5 " "
	100.0 " "

For purposes of discussion, the industrial applications of tungsten may be grouped as follows:

I. Ferrous Alloy Tool Steels (after Gill)
  1. Oil Hardening Non-Deforming Steels
  2. Tungsten Finishing Steels
  3. Low Alloy Tap Steels
  4. Tungsten Chisel Steels
  5. Wortle Die and Self-Hardening Steels
  6. Die Steels for Hot Work
  7. Miscellaneous Types
    Die Steels for Cold Work
    Graphite Steels
  8. High Speed Steels

II. Ferrous Alloys, Other Than Tool Steels
  1. Tungsten Magnet Steels
  2. Tungsten in Stainless and Heat-resisting steels
  3. Commercial Ferrous, Tungsten Alloys

III. Non-Ferrous Alloys
  1. Stellite (Co-Cr-W)
  2. Tungsten-Molybdenum
  3. Nickel-Tungsten
  4. Tungsten-Cobalt
  5. Copper-Tungsten and Silver-Tungsten
  6. Tungsten-Nickel-Copper
  7. Lead-Tungsten

8. Acid-resisting
9. Miscellaneous
IV. Tungsten Carbides
V. Electrical Equipment
VI. Tungsten Compounds
  1. Tungsten Bronzes
  2. Colors
  3. Miscellaneous
VII. Miscellaneous Applications
VIII. Pure Tungsten of Commerce

General Effect of Alloying Elements. We are here concerned mainly with the alloying effects on steels of over 0.50 carbon.

In the alloying of tool steel, tungsten possesses a stabilizing effect on the alpha and delta phase, solid solution (ferrite). It narrows the range of stable austenite when present in large amounts unless compensated for by such elements as carbon or cobalt the former of which renders a high degree of martensitic hardness at heat treating temperatures. Thus with 11 per cent tungsten in order to render the absence of ferrite some 0.25 per cent carbon is required while with 15 per cent tungsten about 0.35 per cent carbon is necessary.

The alloying elements, titanium, vanadium, tungsten, molybdenum and chromium shift the carbon requirement for eutectoid composition to lower values while they raise the eutectoid temperature. They also alter the shape of the "S Curve" for a Plain Carbon Tool Steel, as per figure (p. 299), which shows the "S-curve" for the decomposition of austenite in 18 per cent tungsten, 4 per cent chromium, and 1 per cent vanadium high speed steel,* where at room temperature the matrix of the steel if properly quenched is composed of approximately 80 per cent martensite and 20 per cent austenite.

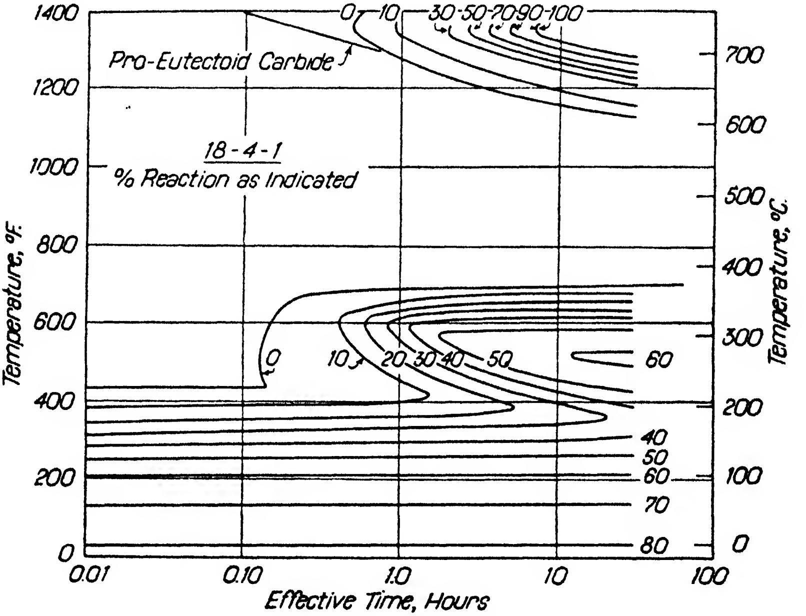
Hardenability. The alloying elements per se can harden and strengthen the ferrite only to a small extent. But their effect on the hardenability of the steel is important. This effect is strong with chromium, molybdenum and vanadium, but moderate with tungsten. The most important role played by them is in slowing down the rate at which austenite changes to pearlite, that is even with a slower quench, the transformation in a temperature range, where the product is soft, is prevented. Increased hardenability also makes deeper hardening possible, accompanied with less drastic quenching.

Tempering. Alloying elements tend to improve the properties of steel by increasing the permissible tempering temperature. In high speed

---

* Cohen, M., Gordon, M. P., and Ross, R. S., "The Kinetics of Austenite Decomposition of High Speed Steel". A.S.M. Reprint No. 30 (1942).

steel, due to the minute dispersement of precipitated carbides, a secondary hardness at comparatively high tempering or operating temperature is effected. Another cause for the production of secondary hardness in alloy steels is due to the decomposition of residual austenite to martensite at between 950° F. (510°) and 1050° F (565°). Red hardness, on the other hand, is due to the reluctance of the complex carbides to coagulate in large sizes. It has been shown that a higher quenching temperature is conducive to a greater stability of hardness at reheating temperatures. Thus, with a 1.5 per cent carbon steel containing 8 per cent tungsten, the Rockwell



"S-curve" for the decomposition of austenite in 18% W, 4% Cr, 1% V high-speed steel. *After Gordon, Cohen and Rose.*

"C" hardness at tempering temperature 1000° F is about 55 if the steel is quenched at 2190°F and is about 45, if quenched at 1470° F."* High tempering temperatures lower a greater quantity of stress than low tempering temperatures.

Restriction of Grain Size. Generally speaking, the carbide forming elements, such as vanadium, tungsten, molybdenum and chromium tend to restrict grain growth in the steel. It has been shown that grain growth is attendant upon the progressive solution and the disappearance of the

---

* Hondremont, Bennek Schrader: *A. I. M. E.* (1934), T. P. 385; *Metals Tech.*, 1 Dec. (1934). No. 8, "Hardening Power and Tempering of Steels containing Carbides of Low Solubility—Especially Vanadium Steels".

carbide particles in certain temperature range; but it is a matter of difficulty to indicate the order of effectiveness of the carbide forming elements in restricting grain growth. However, according to J. G. Gill* "some grain size examination after quenching temperatures of 1600 and 1725° F (870 and 940°), using an 0.85 per cent carbon steel containing 0.30 per cent of alloying elements leads to the following qualitative order of decreasing effectiveness: 1. Vanadium, 2. Tungsten, 3. Molybdenum, 4. Chromium."

Manufacture of Tungsten Steel. In 1927, Lantsberry[3] made the following statement regarding the manufacture of high-speed steel by the crucible process: "Sheffield practice has invariably been to introduce the tungsten from tungsten powder rather than from ferrotungsten. Experience has shown that the use of ferrotungsten does not produce such reliably uniform results as the use of powder because of the variation in the composition of ferrotungsten. These variations will not affect the process of electric melting to anything like the same extent, because of the refining operations effected by this process. In the crucible-melting process it is not so much that tungsten powder makes better high-speed steel, but that it gives a much more uniform product over a long period of time. The melting losses are 10 to 12 per cent of the tungsten, and 30 to 40 per cent of the vanadium added, while the loss of chromium is practically nil."

With the reference to the manufacture of tungsten steel in the electric furnace Sisco[4] writes: "Two forms of tungsten are available, the ferroalloy and tungsten metal or powder. The ferroalloy should always be used. Tungsten powder melts between 6000 and 6200°F (about 3400°). The average temperature of the bath in the final period is 3000 to 3200° F. (1650 to 1760°), not nearly high enough to effect quick solution of the powder. The ferroalloy on the other hand melts between 3500 and 3700° F (1925 and 2040°) which makes its solution in the bath very much easier. In addition, and this is most important, ferrotungsten has a much lower specific gravity than the powder. Therefore, it does not settle to the bottom of the bath so readily as the powder. This settling of the powder is especially bad as it drags considerable chromium with it."

Arthur Linz has patented a novel method of introducing tungsten in ferrous alloys [U. S. Patent 2,282,486 (1942)]. Powdered tungstic oxide (WO_3) is mixed with about one-tenth of its weight of still-pitch and this mixture is formed into uniform briquettes, each of which may contain five pounds of tungsten. Where tungsten dioxide (WO_2) or any of the suboxides is used, a lesser proportion of carbonaceous material may be employed. The briquettes are charged in the electric furnace and brought to the proper temperature in the usual manner.

---

* Gill, J. P. "Tool Steels" American Society for Metals, 1944, p. 268.

Arthur Linz has patented another novel method of introducing tungsten in ferrous alloys [U. S. Patent 2,302,616 (1942)]. The tungstic oxide used is first partially reduced in a beehive or coke oven until the product contains mostly tungsten dioxide, with some tungsten monoxide and metallic tungsten. This material is then briquetted with not more than 0.25 per cent carbon and 5 to 70 per cent iron particles. It is claimed that when large percentages of tungsten are needed for the manufacture of high-tungsten alloys, briquettes made in this way do not produce a boil which is the case when briquettes made according to the previous patent just described are used.

The Crucible Process.[5] "Practically all of the high-grade steel suitable for tools was formerly made by the crucible process, but this method has been almost entirely superseded by the electric-furnace process, at least in America. As many writers have pointed out, no refining takes place in crucible melting, while the electric-furnace process permits of considerable refining. Consequently, the purity of crucible-melted steel depends almost entirely on the purity of products charged, and it is imperative to use only materials of the highest purity, while raw materials of lower purity and lower cost can be used in the electric furnace to produce steel with a composition and quality comparable with that of the best crucible steel."

According to Lantsberry[6], a typical charge used in Sheffield for producing 18 per cent tungsten high-speed steel is as follows:

"28¼ lb.	Swedish bar ends
9 lb.	Small Swedish scrap
9¼ lb.	Washed metal
11½ lb.	Tungsten powder
3 lb.	Chromium metal
30½ oz.	Ferrovanadium (35 per cent)

"The melting operation takes from 4 to 4½ hr. Fifteen minutes before melting is complete, from 1 to 3 oz of ferro-manganese and about 2 oz of ferrosilicon are thrown into the pot. When melting is complete, the pots are lifted from the furnace and a pill of aluminum is added to each pot. They are then teemed singly or the contents of a predetermined number of pots are combined according to size of the ingot required."

The Electric Furnace Process. In his book "The Manufacture of Electric Steel," Sisco[7] discussed the melting of high-speed steel as follows:

"Furnace men always use as much high-speed scrap as possible in the heat, up to two-thirds or even three-fourths of the charge. There is nearly always high-speed scrap available and at a price that makes it a cheaper practice than if plain scrap and ferrotungsten are used. To recover all of the alloys, melting must be without oxidation. After the bath is molten, and the slag deoxidized and free from tungsten, chromium, and vanadium, a test is taken and sent to the laboratory where carbon, manganese, chromium, vanadium, and tungsten are determined. In some shops, a sample of slag is taken at the time and analyzed for tungsten to make sure that all of this element has been reduced from its oxide and has gone back into the metal.

"While the analysis is being made (this will take from 45 min to $1\frac{1}{2}$ hr), the slag is made carbide. As soon as the analysis results are received, the ferrotungsten and ferrochromium are added. Part of the ferrovanadium may also be added here, but it is considered better practice and safer to add this ferroalloy toward the end of the heat. As soon as the ferrotungsten and ferrochromium are melted, 20 min is sufficient with a very hot bath, the heat is well stirred, and the final tests taken. These are drilled and sent to the laboratory where carbon, manganese, tungsten, chromium, and vanadium are again determined. On this, the final analysis, chromium, tungsten, and manganese should be within the required limits, the carbon very nearly up to the minimum, and the vanadium content a little below that of the average in the scrap.

"The ferrosilicon is now added, washed metal is also added if necessary to increase the carbon, and the heat is stirred. All of the ferrovanadium is now rapidly shoveled in and after 20 to 30 min, in which temperature is adjusted, the ladle is placed in position and the heat tapped."

Sisco recommended that an electric furnace heat of high-speed steel be tapped at a temperature of approximately 1625° and teemed at a temperature between 1580 and 1590°.

The Electric Arc Furnace*. This furnace today is our largest producer of high grade tool steel. The units used for making tool steel range from about 1 to 10 tons capacity and will tap a heat about every five or six hours. A diagrammatic view of a typical furnace is given in the figure (p. 303). The basic electric arc furnace can remove both phosphorus and sulfur to extremely low values.

"These furnaces are charged almost entirely with carefully selected steel scrap or pure iron of known analysis. They never start out with a charge of pig iron. If the charge consists of cold materials, it is spoken of as cold melt electric furnace steel to distinguish from the big production practice of charging the electric furnace with molten steel previously melted in an open hearth furnace. The slower and more expensive cold melt practice is almost universally used for making fine tool steels.

The Coreless Electric Induction Furnace. "This is the newest type of furnace used for making high grade tool steel, and is illustrated in the

---

* Taken from "Tool Steel Simplified" by Frank R. Palmer, The Carpenter Steel Co., Reading, Pa. (1937).

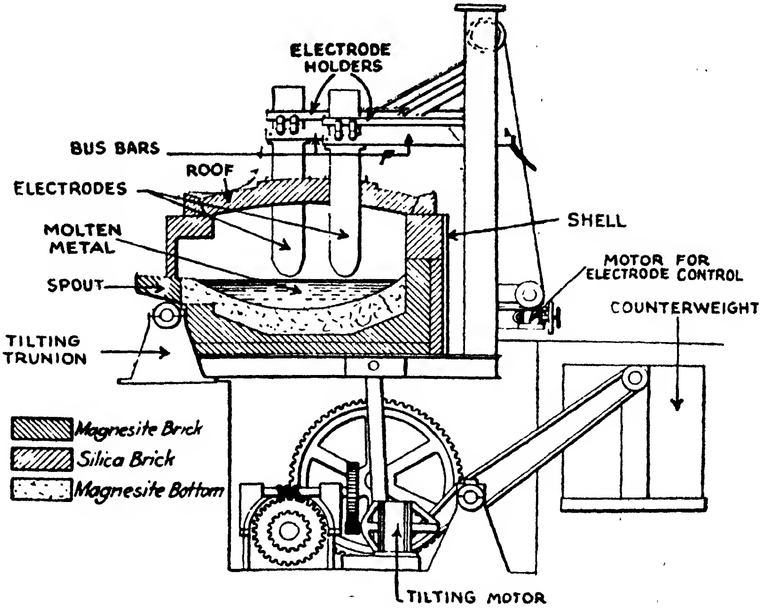
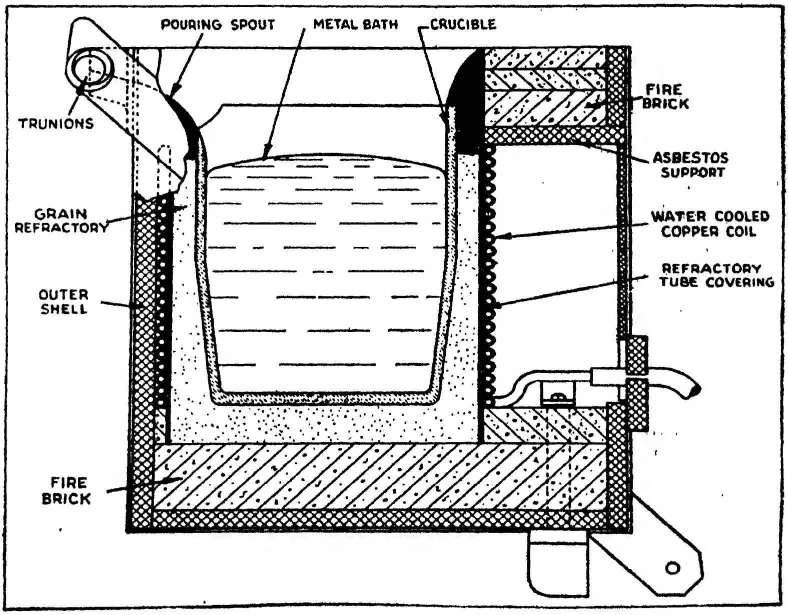


Diagram of electric arc furnace. *Courtesy American Society for Metals.*



Section of high frequency coreless induction furnace. *Courtesy American Society for metals.*

figure (p. 303). It operates on the principle of an electric transformer. The primary current is a high frequency alternating current, and this is passed through a water cooled copper coil which surrounds the melting crucible. The crucible is filled with carefully selected steel scrap which acts as the secondary of the transformer. When the high frequency current passes through the copper coil, currents are generated in the pieces of scrap causing them to become very hot and in a comparatively few minutes the entire charge is melted.

This furnace does something that no other tool steel melting furnace can do—the steel is stirred and mixed continuously by the action of the induced electric currents.

The capacity of induction furnaces ranges from a few hundred pounds to five or six tons and they are capable of pouring a heat about once every hour. There is, of course, no oxidizing condition present so that high quality dead-killed steel can be made just the same as in the electric arc furnace. The induction furnace, as used today, has little if any capacity to eliminate phosphorus or sulfur so that these impurities must be kept very low in the charge of raw materials. Excepting for the method of heating, the induction furnace makes steel on much the same principle as the old-fashioned crucible furnace.

Manufacture of Tool Steels. "Tool steel is usually cast in square or octagon ingots ranging from 6″ to perhaps 20″ in diameter. The first operation a tool steel ingot is to convert it into a billet by a process known as cogging. This may be done by hammering, rolling or pressing. Some of the highly alloyed steels, like high speed steel, cannot be cogged very satisfactorily on a rolling mill and these analyses are therefore hammered—whatever the ingot size may be. Practically all bars of tool steel must be annealed before they are sold. To avoid scaling, much of this work is done by packing the bars in large pipes with a non-oxidizing substance like cast iron borings. During heating for cogging, rolling and annealing, it is virtually impossible to prevent a certain amount of carbon from being oxidized from the outside skin of the bar. Decarburization is one of the reasons why steel makers recommend removing a certain amount of metal from the surface of the bar in making a tool. A considerable quantity of tool steel is purchased in cold drawn bars for the manufacture of drills, taps and similar tools. For this purpose, hot rolled, annealed bars (or coils) are pickled to remove all scale and are then drawn through a die which is perhaps $\frac{1}{16}$″ smaller than the diameter of the bar. Although the vast majority of tools are made from pieces cut from bars, the tool maker has frequent need for large discs or rectangular pieces of odd dimensions. These are generally hammered.

I. FERROUS ALLOYS TOOL STEELS

I. 1. **Oil Hardening Non-Deforming Steels (Low Alloy Types)**

	C	Si	Mn	W	Cr	V	Mo
a. Manganese type	0.95	0.25	1.20	0.50	0.50	0.20	
b. Tungsten type	1.20	0.25	0.25	1.3–1.8	0.75	0.25 (optional)	0.25 (optional)
c. Chromium type	0.90	0.25	0.25	0.45	1.60		

The properties which render this group adaptable for general tool and die purposes are:

1. Low movement in hardening
2. High as quenched hardness
3. High hardenability from low quenching temperature
4. Freedom from cracking on quenching intricate sections
5. Maintenance of a keen edge for cutting purposes.

The uses of these steels include: taps, reamers, broaches, bushings, plug ring and thread gauges, thread rolling dies, master tools used in the shaping of form tools, stamping and blanking dies, punches and forming dies.

The manganese content of type (a) makes it possible to harden in oil from low temperatures. The presence of tungsten and chromium renders higher temperatures heating possible without detrimental grain growth.

The tungsten type (b) is good for roll turning tools, paper and wood working knives and in tools for finishing purposes.

The chromium type (c) posseses some of the characteristics of type (a) and is poorer in wear resistance than type (b).

I. 2. **Tungsten Finishing Steels**

	C	Si	Mn	W	Cr		Mo
Type a.	1.35	0.25	0.25	3.0–4.0			
Type b.	1.35	0.25	0.25	3.0–4.0	0.50	or	0–0.50
Type c.	1.35	0.25	0.25	3.0–4.0	0.50–1.00	or	0.50–1.00

The finishing steels possess extreme wear resistance or abrasion resistance, whereby a keen cutting edge can be retained. Their main use is therefore for small tube and wire drawing dies. Other uses are for sizing plugs and gauges, brass cutting tools, roll turning tools, forming tools and forming or piercing punches.

The core of tungsten finishing steels hardens better than that of plain carbon steels. Steels of type (c) are generally hardened at slightly higher temperatures than those of type (a).

I. 3. **Low Alloy Tap Steels**

C	Si	Mn	W
1.25	0.25	0.25	1.50

On account of its hardness and good wear resistance, this steel is applicable for fine edged cutting tools such as taps, small broaches, and reamers. It is closely allied to the tungsten finishing steels of Class (2) and to type b of Class (1). This kind of tap steel has been more widely used in Europe and England than in the United States.

I. 4. Tungsten Chisel Steels

	C	Si	Mn	W	Cr	V
Type a.	0.50	0.25	0.25	2.10	1.50	0.25
Type b.	0.40	0.90	0.25	2.00	1.00	
Type c.	0.50	0.25	0.25	1.00	1.00	
Type d.	0.50	1.00	0.25	1.00	1.00	

The Tungsten Chisel Steels are used for shock resisting tools as well as for hot working purposes and are better than silico-manganese steels because they show higher impact values than the latter. Type (a) because of its having greater amount of chromium is preferred for hot working applications, requiring deep hardening as in the case of larger sizes. Type (d) was widely known as the 1-1-1 type. The addition of vanadium in type (a) is intended as a grain refiner.

I. 5. Wortle Die and Self-Hardening Steels

	C	Si	Mn	W	Cr
Type a.	2.25	0.25	0.25	0.50	0.50
Type b.	2.00	0.25	0.75	4.50	2.00
Type c.	2.00	0.25	0.75	3.50	—
Type d.	2.25	0.25	1.50	11.00	2.00
Type e.	2.00	0.25	1.50	3.75	3.75

These steels are characterized by a comparatively high percentage of carbon, approximately 2 per cent. The amount of tungsten present determines the duties of the wortles. "Soft wortles are used principally for drawing soft wire rounds and shapes; hard wortles for drawing fine wire".

The Wortle Die Steels and Self-Hardening steels nowadays find little application and are interesting only as forerunners of our modern high alloy steels. There have been developed as many as about fifty types of such steels and the above five types are selected as representative.

I. 6. Die Steels for Hot Work

	C	Si	Mn	W	V	Cr	Ni	Mo
a. 6.00% Molybdenum Type	0.35	0.25	0.25	1.00	0.75	3.50		6.25
b. Chromium-Tungsten Type	0.40	0.90	0.25	4.50-5.50		5.00		
c. Chromium-Tungsten-Molybdenum Type	0.35	0.90	0.25	1.25	0.25 (optional)	5.00		1.25-1.75
d. 7.00% Chromium-7.00% Tungsten Type (A)	0.35	1.50	0.60	7.50		7.50		
(B)	0.45	1.50	0.60	7.50		7.50		
(C)	0.60	0.90	0.60	7.50		7.50		

e. 10.00% Tungsten-3.00% Chromium Type	0.30	0.25	0.25	9.00–11.00	0.40	3.25		
f. 10.00% Tungsten-2.00% Chromium Type	0.45	0.25	0.25	11.00	0.40	2.00		
g. 15.00% Tungsten Type (A)	0.30	0.25	0.25	15.00	0.40	2.75		
(B)	0.45	0.25	0.25	15.00	0.40	2.75		
h. Nickel-Tungsten Type (A)	0.33	0.25	0.25	14.00		4 00	2.50	2.10
(B)	0.33	0.25	0.25	11.00		3.00	1.50	

The die steels for hot work possess the important properties of resistance to erosion or wear. at the working temperature, resistance to shock, resistance to the formation of cracks at the surface, etc. The tungsten hot working steels generally retain considerable hardness up to 1150° F. (620°) while those of chromium only up to 800° F. (425°). These steels cannot generally stand rapid cooling water in operation without danger of breaking.

Type (a) is specially resistant to "fire checking". The molybdenum content is responsible for rapid grain growth which confers a better property in the dies for certain hot working applications than fine-grained structure. Type (a) may be considered as a substitute for type (g).

Types (b) and (c) are now widely used for all general hot working operations, such as die casting dies, forging dies, punches, piercers, and mandrels and shear blades for hot work. Type (b) is, on account of its high content in tungsten, superior to type (c) in greater wear resistance and prevents softening at high temperatures but does not possess as great a hardenability as type (c) which contains molybdenum in addition.

Steels of type (d) can be used both for hot and cold work. Steels of this type with lower carbon content are specially adaptable for cold work. On account of the high chromium content, these steels do not scale so much at heat treatment temperature as the tungsten hot working types. Type (d) (C) with higher carbon content, 0.60 per cent, can be used for razors, high grade pocket knives, balls, ball races, propeller shafts, valve parts et cetera.

Types (e) to (h) are sometimes called semi-high speed steels, containing, as they do, low percentages of carbon and from 9 to 15 per cent tungsten together with 2.00 to 4.00 per cent chromium, 0.40 per cent vanadium, and sometimes 2.00 per cent molybdenum and 2.00 per cent nickel as per type (h). The content of nickel confers in steels of this type the property of highest working range among the tungsten hot working steels.

I. 7. Miscellaneous Types

High Carbon, High Chromium Die Steels. C 2.25, Si 1.00, Mn 1.00, W 1.00, Cr 11.50. These steels are used for cold work. The brittleness of this type of high carbon steel is counteracted by the presence of high silicon and tungsten.

Graphite Steels. C 1.50, Si 0.65, Mn 0.30, W 2.80, Mo 0.50. The hardenable, free machining quality of these steels is due to the high carbon content plus a relatively high silicon content.

I. 8. High Speed Steels

Class A—Tungsten Types.

	C	W	Mo	Cr	V	Co
a. 18-4-1	0.50-0.80	18.00	—	4.00	1.00	—
b. 18-4-2	0.80	18.00	0.80	4.00	2.00	—
c. 14-4-2	0.75	14.00	—	4.00	2.00	—
d. 18-4-3	0.95	18.00	—	4.00	3.00	—

Class B—Tungsten-Cobalt Type.

	C	W	Mo	Cr	V	Co
a. 18-4-1 + 5% Co	0.75	18.00	0-0.80	4.00	1.00	5.00
b. 18-4-2 + 8% Co	0.75	18.00	—	4.00	2.00	8.00
c. 14-4-2 + 5% Co	0.75	14.00	--	4.00	2.00	5.00
d. 20-4-2 + 12% Co	0.75	20.00	—	4.25	1.75	12.00

In the above list only the principal representative types of tungsten high speed steels are given, reserving the molybdenum types of high speed steels to be discussed in the chapter on Substitution of Tungsten. The basic type of high speed steel is of course the 18.00 per cent tungsten, 4.00 per cent chromium, 1.00 per cent vanadium steel, the so-called 18-4-1 type. With a lower carbon content between 0.50 and 0.60 per cent, this type of steel can also be used as a die material. The diagram below shows the relation between the weight and atomic percentages of the principal alloying elements found in an 18-4-1 high speed steel, from which it can be seen that the number of chromium atoms present is almost about the same as that of the tungsten atoms and that the carbon atoms present amount to more than half of tungsten atoms.

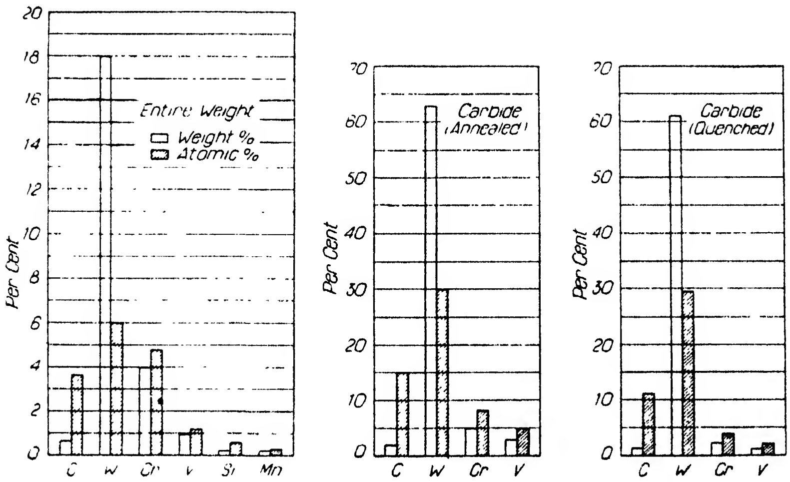
Red Hardness. The main characteristic of high-speed steel tools is that they maintain a sharp cutting edge at working temperatures far above those that ruin carbon-steel tools. This property is generally known as "red-hardness" which develops at 700-800°. The cause of "red-hardness" has not yet been explained satisfactorily.

According to Bain and Jeffries* "The cause of the red hardness of high-speed steel might be briefly stated as follows: The changes which cause martensite of carbon steel to soften are grain growth of the ferrite and growth of the carbide particles above critical size. Similar changes in high-speed steel take place only at a red heat. The outstanding reasons for the retention at red heat of fine grains in the ferrite of high-speed steel are the increased resistance to growth due to the elements in atomic dis-

---

* Bain, E. C. and Jeffries, Z.; "Cause of Red Hardness of High-Speed Steel", *Iron Age*, **112**, 805-810 (1923).

persion in the ferrite and copious presence of obstructing carbide particles. The reason for retention at red heat of carbide particles of critical size is the great stability of the iron-tungsten carbide and the large size of the tungsten atom. The great stability of this double carbide forces its formation to the exclusion or elimination of other carbides when the necessary atoms are available. The large size of the tungsten atom prevents its diffusion in the ferrite space lattice until a temperature corresponding to a red heat is reached. The double carbide is an intermetallic compound which owes its existence entirely to crystallization. The formation of a particle of this carbide, therefore, requires a number of tungsten atoms which must be supplied by diffusion through the ferrite lattice."



Relationship between the atomic and weight percentages of the elements occurring in an 18% W, 4% Cr, 1% V, 0.70% C, 0.25% Si, 0.25% Mn high-speed steel. *Letf:* Relationship for entire steel. *Middle:* Relationship for carbide; data from chemical separation of carbide from annealed steel. *Right:* Relationship for carbide; data from chemical separation of carbide from hardened steel. *After J. P. Gill.*

Classification[9] of high-speed steels by manufacturer and trade name is as follows:

18% W, 4% Cr, 1% V

Manufacturer	Brand
Allegheny-Ludlum	LXX
Bethlehem	Bethlehem Special HS
Braeburn	Vinco
Carpenter	Star Zenith
Columbia	Clarite
Crucible	Rex AA
Firth-Sterling	Bue Chip
Halcomb	Dreadnaught

Manufacturer	Brand
Jessop	Supremus
Latrobe	Electrite No. 1
Midvale	Two Star
Simonds	Red Streak
Universal-Cyclops	B-6
Vanadium	Red Cut Superior
Vulcan	Wolfram
18% W, 4% Cr, 2% V	
Allegheny-Ludlum	ML
Bethlehem	HV
Braeburn	Twin Van
Carpenter	Super Star Zenith
Columbia	Vanite
Crucible	Rex Super Van
Firth-Sterling	HV Blue Chip
Halcomb	Super Van Dreadnaught
Jessop	Supremus Extra
Latrobe	Electrite No. 19
Midvale	Two-Star Special
Simonds	Lockport Special
Universal-Cyclops	B-9
Vanadium	EVM
Vulcan	Super HS Steel
18% W, 4% Cr, 3¼% V	
Latrobe	Electrite Vanadium
18% W, 4% Cr, 1% V, 4% Co	
Allegheny-Ludlum	Panther Special
Bethlehem	Comokut
Crucible	Rex AAA
Halcomb	Baltoc
Jessop	Purple Label
Latrobe	Electrite Cobalt
Midvale	Three Star
Simonds	Tunco
Universal-Cyclops	B-7
Vanadium	Red Cut Cobalt
Vulcan	Wolfram Cobalt
18% W, 4% Cr, 2% V, 8% Co	
Allegheny-Ludlum	Super Panther
Braeburn	Bonded Carbide Jr.
Crucible	Rex 18-8
Disston	D-6 Co.
Firth-Sterling	Circle C
Latrobe	Electrite Super Cobalt
Midvale	Four Star
Simonds	Super Cobalt
Universal-Cyclops	B-10
Vanadium	Red Cut Cobalt B
22% W, 4% Cr, 1.50% V, 12% Co	
Braeburn	Bonded Carbide
Crucible	Rex 440
Latrobe	Electrite Ultra Cobalt
Midvale	Five Star
Vanadium	Grey Cut Cobalt
14% W, 4% Cr, 2% V	
Bethlehem	Extra Special HS
Braeburn	Gyro
Crucible	Rex Champion
Firth-Sterling	Star Blue Chip
Halcomb	Super Dreadnaught
Jessop	Jessco
Latrobe	Electrite Uranium

Manufacturer	Brand
Midvale	One Star
Universal-Cyclops	B-42
Vulcan	No. 14
14% W, 4% Cr, 2% V, 5% Co	
Braeburn	Cobalt
Carpenter	Gold Star
Columbia	Maxite
Crucible	Rex 95
Halcomb	999
Jessop	Jessco B
Latrobe	Electrite Uranium B
Midvale	Three Star
Universal-Cyclops	B-8

Effect of Alloying Elements in High Speed Steel.

Carbon. If the 18-4-1 type high speed steel contains lower carbon content, such as 0.50 to 0.60 per cent, maximum hardness is not obtained on account of the presence of ferrite. However this type finds wide application as hot die materials. With an increase of carbon content the amount of complex carbide present in the steel increases, conferring an increased wear resistance to the steel.

Tungsten. Tungsten as an alloy element in tool and die steels, occurs partly as a solute in gamma iron and partly as Fe_3W_3C or Fe_4W_2C—better expressed as* $(FeW)_6C$—in high tungsten steel. A small amount of tungsten may be dissolved in iron carbide (Fe_3C), and Fe_3C and WC may be present together in varying proportions. Apparently two tungstides are formed Fe_2W and Fe_3W_2. Grossman and Bain[2] point out that in low-carbon, high-tungsten alloys, the double carbide $(FeW)_6C$ is formed rather than the tungstide, and only the surplus tungsten remaining would produce the tungstide and saturate the ferrite.

Chromium. The use of chromium seems to effect a compromise between hardness and toughness in high speed steel. The cause of secondary hardness in high speed steel is in part due to the presence of chromium in the complex carbide. Chromium appears to effect the reduction of oxidation and scaling during heat treatment of the steel.

Vanadium. Vanadium is added principally for the following reasons: (1) for producing very fine grain size; (2) because the stability of V-rich carbides increases with temperature; (3) to increase ductility and toughness.

Molybdenum. The effect of molybdenum will be discussed in Chapter VIII.

*Cobalt***. "The main effect of cobalt in high speed steel is to increase

---

* This compound crystallizes in the complex cubic system with 112 atoms per unit cell and a lattice parameter of 11.04 A°. J. P. Gill, "Tool Steels", p. 432.

** Gill, J. P., "Tool Steels", p. 512–513, p. 515. American Society for Metals, Cleveland, Ohio, 1944.

the hot hardness and thus to increase the cutting efficiency when high tool temperatures are attained during the cutting operation. Cobalt steels, are, therefore, good on roughing or hogging cuts, but they are not superior for fishing cuts where high tool temperatures are not attained. The cobalt types will usually perform quite well when cutting materials which have discontinuous chips, such as cast iron or non-ferrous metals. The necessity of using deep cuts and fast speeds or of cutting hard and scaly materials justifies the use of cobalt high speed steels."

"Cobalt in high speed steel raises the melting point and thus higher heat treating temperatures are permissible without appreciable grain growth occurring. This enables a greater solution of the tungsten, chromium, vanadium, and carbon in the austenite which, together with the cobalt present in the matrix, causes a greater amount of retained austenite (said by Michel and Benazet to be more stable austenite) a greater amount of secondary hardness and a greater amount of red hardness."

The principal carbide present is Fe_4W_2C or Fe_3W_3C. Chromium and vanadium are probably associated with tungsten in the double carbides, which have the general formula $(Fe \cdot W \cdot Cr \cdot V \cdot)_6C$; but cobalt does not form carbide. Hence, 1 per cent of chromium and vanadium are assumed to be structurally equivalent to about 0.5 per cent and 5.0 per cent tungsten, respectively.

FERROUS ALLOYS OTHER THAN TOOL STEELS

II. 1. Tungsten Magnet Steels

Before 1917, when Honda and Takagi discovered the use of cobalt in magnet steels, the best permanent magnets were made from steel containing 5–7 per cent tungsten with 0.65–0.75 per cent carbon. The total tungsten consumption for permanent magnets is now very small.

A comparison of these two types of magnet steels is shown below:

	Composition (%)	Treatment	Specimens	Remanence (gauss)	Coercive Force (oersteds)
Tungsten Magnet Steel	C, 0.6 W, 6.0	Watter quenched from 850° C		10,000–10,500	60
Cobalt-chromium-tungsten alloys	C, 0.4–0.8 Co, 35–40 W, 5–9 Cr, 1.5–3	Final hardening in oil from 950° C.	KS, 1	11,560	226
			2	10,570	221
			3	10,405	245
			4	7,790	257

The cobalt-chromium-tungsten alloys are necessarily expensive and are mostly used for small magnets, *e.g.*, in moving-coil loud speakers.

Some of the commercial types of tungsten-containing magnet steels are[8]:

Type of Steel	Nominal Composition (%)						Nominal Magnetic Properties		Hardening Temp. (°F)	Quenching Medium	Manufacturer
	C	Mn	Cr	W	Co	Mo	Br (gauss)	Hc (oersteds)			
W	0.70	0.30.	2 00	5.50	—	—	10,000	65	1550	Water	Universal Steel Co. Bethlehem Steel Co. Halcomb Steel Co. Carpenter Steel Co. Ludlum Steel Co. Simonds Saw and Steel Co.
W-Cr	0.70	0.50	0.50	6.00	—	—	9,000	70	1525	Oil	Universal Steel Co. Halcomb Steel Co. Simonds Saw and Steel Co.
Co	0.90	0.35	4.75	1.25	8.50	—	7,500	120	1650	Oil	Halcomb Steel Co
	0.90	0.30 to 0.85	3.50 to 5.75	3.75 to 7.00	35.00 to 41.00	—	9,700	235	1700	Oil	Bethlehem Steel Co Halcomb Steel Co. Carpenter Steel Co. Simonds Saw and Steel Co.
Co-W	0.85	0.50	2.00 to 5.00	8.75	17.00	—	9,000	165	1750	Oil	Bethlehem Steel Co. Halcomb Steel Co. Carpenter Steel Co. Simonds Saw and Steel Co.

II. 2. Tungsten in Stainless and Heat-resisting Steels.*

The addition of tungsten in stainless and heat-resisting steels confers an increased strength at elevated temperatures as well as a slight increase in over-all corrosion resistance. The following types of these steels may be mentioned:

(a) Steel containing 5 per cent chromium, 0.25 per cent maximum carbon and 1 per cent tungsten, finds wide use as distilling tubes for oil refineries.

(b) Steel containing 7.3 per cent chromium, 0.45 per cent carbon, 3.5 per cent aluminum, and 1 per cent tungsten, has been suggested as a valve material for internal-combustion engines.

(c) Steel containing 12 per cent chromium, 2 per cent nickel, 0.12 per cent carbon, 3 per cent tungsten, finds wide use for bolts and turbine materials.

(d) Steel containing 14 per cent chromium, 1 per cent nickel, 1 per cent carbon, 2 per cent silicon, and 3 per cent tungsten, finds some use as a valve steel.

(e) Steel containing 14 per cent chromium, 14 per cent nickel, 0.40 per cent to 0.50 per cent carbon, 0.30 to 0.80 per cent silicon, and 1.75

---

* Tungsten Steel," pp. 65–78, Molybdenum Corporation of America, Pittsburgh.

to 3.00 per cent tungsten, is most widely used for exhaust valves in United States aircraft engines.

(f) Steel containing 15 per cent chromium, 25 per cent nickel, 0.45 to 0.50 per cent carbon, up to 2 per cent silicon, 3 to 4 per cent tungsten, has been widely employed by European manufacturers as an exhaust-valve material.

(g) The typical stainless steels of 18-8 compositions to which tungsten is added, find use in applications where high creep strength is required. The compositions of some of these steels are as follows:

Steel	C %	Mn %	Si %	Cr %	Ni %	W %
1	0.34	0.48	0.85	18.51	7.78	3.09
2	0.38	0.68	1.21	18.72	9.74	3.72
3	0.30	0.52	1.46	17.70	7.00	4.23

II. 3. Commercial Ferrous Tungsten Alloys

The following is a list of some of the commercial ferrous tungsten alloys, other than the tungsten tool steels already described[12]:

Name	Wolfram	Composition	Reference	Uses
Acid Resisting	6.2	10 Cr, 30 Ni, 40.8 Fe, 1.55 Mn, 0.45 Si	Campbell "A List of Alloys" A.S.T.M. Proceedings Vol. 30 Part 1 (1930)	Chemical apparatus, acid resisting vessels and tanks
Acid Resisting		15 Cr, 53 Ni, 23 Fe, 1.25 Mn, 3.75 Si	Campbell "A List of Alloys" A.S.T.M. Proceedings Vol. 30 Part 1 (1930)	Chemical apparatus
Allegheny 33W	2.5-3.5	12–15 Cr, 0.12 max. C, bal. Fe	Allegheny Steel Company	Chemical engineering equipment. High temperature service
Allegheny 66W	2.5-3.5	15–18 Cr, 0.12 max. C, bal. Fe	Allegheny Steel Company	Chemical engineering equipment. High temperature service
Allegheny 46 Tungsten		0.35 max. C, 5-7 Cr, W, bal. Fe	Allegheny Steel Company	Corrosion resistant parts
Atsina		C, W, bal. Fe	Ludlum Steel Company	Magnets, electrical machinery
Bario	15.4	21.4 Cr, 57.4 Ni, 1 Fe, 0.3 C	Campbell "A List of Alloys" A.S.T.M. Proceedings Vol. 30, Part 1 (1930)	Resistor elements
Bedel INO 31		C, 14 Cr, 15 Ni, W, Mo, Bal. Fe	Bedel & Cie	Valves operating up to 900°
Bedel INO 33		C, 25 Ni, 10 Cr, W, bal. Fe	Bedel & Cie	Valves operating to 900°
Bedel M.G.B.C.	8	C, 35 Co, bal. Fe	Bedel & Cie	Magnets
Bedel M.G.B.S.	5-6	C, Cr, bal. Fe	Bedel & Cie	Magnets
Bethlehem 4-6 Cr.		C, 5 Cr, with or without W or Mo, bal. Fe	Bethlehem Steel Co.	Chemical engineering equipment, refinery parts
Bethlehem No. 1 Permanent Magnet	6	C, bal. Fe	Bethlehem Steel Co.	Magnets
Bohler Me	5.8	0.70 C, 0.25 Max. Si, 0.34 Mn, bal.Fe	Bohler Bros. & Co.	Magnets
Bohler ME-6		C, W, bal. Fe	Bohler Bros. & Co.	Meter magnets

Name	Wolfram	Composition	Reference	Uses
Carpenter V-Chrome Steel		0.4–0.6 C, 4–6 Cr, Mo. or W optional, bal. Fe	Carpenter Steel Co.	Heat resisting parts
Cobalt Magnet Steel (17%)		C, Cr, W, Co, bal. Fe	Halcomb Steel Co.	Permanent magnets
Cobalt Magnet Steel (35%)		C, Cr, W, Co.	Halcomb Steel Company	Permanent magnets
Cooper CA 5	0.8–1.25	4–6 Cr, 0.30 Max. C, 0.4–0.65 Mo, 0.50 Mn, bal. Fe	Cooper Alloy Foundry Co.	Oil refineries, valve fittings
Cooper Stainless S-21W	3.5	0.40 Max. C, 15 Cr, 25 Ni, bal. Fe	Cooper Alloy Foundry Co.	Heat, erosion and corrosion resistant parts
Cristite	17	10 Cr, 3.5 C, 2.5 Mo, bal. Fe	Commercial Alloys Co.	Facing dredger, dipper or shovel teeth and bucket lips, agricultural implements, knives, tools, drills, chisels
Cronite W.X.2		Ni, Cr, Fe, W	Chronite Foundry Co.	For drastic temperature conditions
Crotung	1.0	0.15 C, 0.5 Mn, 0.5 Si, 5.0 Cr, bal. Fe	Climax Molybdenum Corp.	Dies, petroleum still parts
Crusco Steel		C, Cr, W, Co, V, bal. Fe	Crucible Steel Casting Co.	Piercing points, rolling mill plugs, dies, forming rolls
Cyclops K-R K-Rustless	8	0.6 C, 8 Cr, bal. Fe	Cyclops Steel Company	Cutlery, valves, propeller shafts, ball races, dies
Duke's Metal	0.4	81 Fe, 12 Cr, 1.5 C, 4 Co, 0.6 Si, 0.2 Mn	International Critical Tables Vol. II (1927)	Tools, dies, corrosion and heat resisting parts
Elinvar		36 Ni, 12 Cr, W, 0.8 C, bal. Fe, 1–2 Si	Soc. Anon. de Commentry Fourchambault et Decazeville	Watches and chronometers, resistance wire hair springs
Empire No. 25-12W		0.36–0.50 C, W, 25 Cr, 12 Ni, bal. Fe	Empire Steel Castings, Inc.	Heat and corrosion resistant parts
Empire 46		0.13–0.20 C, 5 Cr, Mo or W, bal. Fe	Empire Steel Castings, Inc.	Castings
Empire 2810		C, 28 Cr, 10 Ni, Se, W, bal. Fe	Empire Steel Castings Inc.	Heat and corrosion resistant parts
Empire 2815		C, 28 Cr, 15 Ni, Se, W, bal. Fe	Empire Steel Castings Inc.	Heat and corrosion resistant parts
Enduro 4–6 Cr, "W"	0.75–1.25	0.25 Max. C, 0.5 Max. Mn, 4–6 Cr, bal. Fe	Republic Steel Corp.	Corrosion resisting parts
Era A.T.V.		C, Cr, Ni, Si, W, bal. Fe	Hadfields, Ltd.	High duty I.C. engine valves, super charger rotors
Era A.T.V.	3.3	13.4 Cr, 22.6 Ni, 1.5 Mn, 1.8 Si, bal. Fe	Campbell "A List of Alloys" A.S.T.M. Proceedings Vol. 30 Part 1 (1930)	Heat and corrosion resisting parts
E.S.C. Immaculate No. 6 Firth-Vickers Immaculate No. 6	4.0	0.35–0.45 C, 1.5–2.5 Si, 1.0–1.5 Mn, 25–30 Ni, 14–16 Cr, bal. Fe	English Steel Corp. Ltd. Firth-Vickers Stainless Steels Ltd.	For use at high temperature, turbine blades, exhaust valves, fans, grids
E.S.C. Immaculate No. 9 Firth-Vickers Immaculate No. 9	2.0–2.5	0.40–0.50 C, 1.2–1.5 Si, 0.5–0.6 Mn, 10–12 Ni, 12–14 Cr, bal. Fe	English Steel Corp. Ltd. Firth-Vickers Stainless Steels Ltd.	Exhaust valves for gasoline and oil engines
Fermet	1	4 Cr, 18 Ni, 2.2 Mn, 0.3 Cu, 0.35 C, bal. Fe	Campbell "A List of Alloys" A.S.T.M. Proceedings Vol. 30 Part 1 (1930) International Critical Tables (Vol. II) 1927	Corrosion resisting parts

Name	Wolfram	Composition	Reference	Uses
Firth-Brown J-185		C, High Ni, Cr, W, bal. Fe	Thos. Firth & John Brown Ltd.	Furnace parts, mechanical stokers, exhaust valves, heat treating boxes
Firth-Brown P-281 (Tungsten Magnet) Atlas Tungsten Magnet	6	C, bal. Fe	Thos. Firth & John Brown Ltd.	Aircraft and automobile magnetos, telephone, telegraph and radio apparatus
Firth-Brown P-282 (Tungsten Chrome Magnet)	6	C, Cr, bal. Fe	Thos. Firth & John Brown Ltd.	Aircraft and automobile magnetos, telephone, telegraph and radio apparatus
Firth-Vickers (H.R. Crown Max)		C, Ni, Cr, W, bal. Fe	Thos. Firth & John Brown Ltd., Firth-Vickers Stainless Steels Ltd.	Furnace Parts, mechanical stokers, exhaust valves, annealing boxes
Firth-Vickers "Immaculate 4W"	4	C, 20 Cr, 8 Ni, bal. Fe	Firth-Vickers Stainless Steels, Ltd	Exhaust valves, turbine blades, furnace parts
G.S.E.		C, Cr, Ni, W, Si, bal. Fe	Deutsche Edelstahlwerke	Valves
Hadfields Era		13-20 Cr, 0.5-1.5 Mn, 7.23 Ni, W, Si, Cu, Mo, Low C, bal. Fe	Hadfields, Ltd.	Chemical plant and engineering applications, domestic utensils and fittings
Halcomb Lo Chro W. Stud	1	0.25 C, 6 Cr, bal. Fe	Halcomb Steel Company	Corrosion resistant parts
Hymax 35% Cobalt Magnet		35 Co, bal. Fe, Cr, W	Edgar Allen & Co.	Magnet steel
Imperial Permanent Magnet	6	C, 6 Cr, bal. Fe	Edgar Allen & Co.	Magnet steel
Imphy A.R.C. 1047		C, 18 Cr, 8 Ni, W, bal. Fe	Soc. Anon. de Commentry Fourchambault et Decazeville	Chemical equipment
Imphy A.T.G.	4	60 Ni, 26 Fe, 10 Cr	Soc. Anon. de Commentry Fourchambault et Decazeville	Gas turbines, internal combustion engines
Industrial Cro-Tung	0.75-1.0	0.30 Max C, 4.5-6.5 Cr, bal. Fe	Industrial Steels Inc	Corrosion resistant parts
Jessup Alloy 104	1.0	0.10-0.20 C, 5 Cr, bal. Fe	Jessup Steel Company	Bolts, bushes, pipes
K. S. Magnet Steel	5-9	30-40 Co, 1.5-3 Cr, 0.35 Mn, 0.12 Si, 0.4-0.8 C, bal. Fe	Campbell "A List of Alloys" A.S.T.M. Proceedings Vol. 30 Part 1 (1930); Internat'l Critical Tables-Vol. II (127)	Tools, magnets
La-Bour R-50 (Modified)	2	8-9 Ni, 23 Cr, 6 Cu, 4 Mo, 0.75 Si, C, 53-54 Fe	La Bour Company	Valves, pump parts
La-Bour R-50	4	55 Ni, 23-25 Cr, 5-6 Cu, 2 Mo, 10 Fe	La Bour Company	Valves, pump parts
La-Bour R-55	2	4 Si, 23 Cr, 6 Cu, 4 Mo, 0.2-0.3 C, 52 Ni, 8 Fe	La Bour Company	Pump parts
Lo Cro 4 6-W	0.75-1.25	0.20 Max C, 4-6 Cr, bal. Fe	Crucible Steel Co. of America; Halcomb Steel Co.	High temperature stud bolts
M.G.N.	5	C, Si, Mn, bal. Fe	Soc. Anon. de Commentry Fourchambault et Decazeville	Permanent magnets, electrical equipment

Name	Wolfram	Composition	Reference	Uses
Maxhete		Ni, Cr, W, Cu, Si, bal. Fe	Edgar Allen & Co.	Burner tubes, pipe unions to withstand superheated steam at 900° and 35 lbs pressure
Maxhete No. 1A		C, Cr, Ni, W, bal. Fe	Edgar Allen & Co.	Furnace parts
Maxilvry "A.W."		C, Cr, Ni, bal. Fe, W, Cu	Edgar Allen & Co.	Welded stainless steel parts
Maxilvry "AWP"		C, Cr, Ni, bal. Fe, Cu, W, Ti	Edgar Allen & Co.	Welded stainless steel parts
Midvaloy Aero-Valve	2	0.60 C, 12.5 Cr, 20 Ni, bal. Fe	Midvale Company	Poppet valves for aeronautic engines, heavy trucks, etc.
Midvaloy ATV-3	4	26 Ni, 14.5 Cr, 1.2 Mn, 0.45 C, bal. Fe	Midvale Company	Exhaust valves, gas turbine rotors
Midvaloy BTG	3.0	60 Ni, 12 Cr, 1.2 Mn, 0.3 C, bal. Fe	Midvale Company; Soc. Anon. de Commentry Fourchambault et Decazeville	Autovalves, cast vessels for chemical industries
Midvaloy HR-1	4	7 Ni, 20 Cr, 0.5 Mn, 0.35 C, bal. Fe	Midvale Company	Valves, blowers, rotors, chain grates for stokers
Otisel K-5 Tungsten		0.13-0.35 C, 5-7 Cr, W, bal. Fe	Otis Elevator Company	Corrosion resistant parts
Permanite		Co, Cr, W, bal. Fe	Brady "Materials Handbook" (1931); Internat'l Critical Tables Vol. II (1927)	Permanent magnet steel
Pyros	5	82 Ni, 7 Cr, 3 Fe, 3 Mn	Soc. Anon. de Commentry Fourchambault et Decazeville	Dilatometric temperature indicating or control devices
Q-Alloy Chrome CN2-A		0.21-0.35 C, W, 16-23 Cr, 7-11 Ni, bal. Fe	General Alloys Co.	Heat and corrosion resistant parts
Rez Istal No. 2 CW		0.13-0.20 C, 16-23 Cr, 7-11 Ni, W, Si, bal. Fe	Halcomb Steel Co.	Heat and corrosion resistant parts
Sandvik 13W 12-C 1	5.5-6.0	0.55-0.75 C, 0.2-0.7 Cr, bal. Fe	Sandvikens Jernverks Aktiebolag	Magnetic parts
Saturn (Cyclops)	3.5	1.25 C, bal. Fe	Cyclops Steel Company	Wire drawing plates, dies, cutting tools, chasers, drills
Sideraphite	4	62 Fe, 23 Ni, 5 Cu, 5 Al	Brady "Materials Handbook" (1931)	Acid resisting vessels and apparatus
Silchrome Wire	3	18 Cr, 3 Si, 0.3 C, bal. Fe	Internat'l Critical Tables Vol. II (1927)	Heat and corrosion resisting wire
Silvanite	8	1.25 C, 4 Cr, bal. Fe	Columbia Tool Steel Co.	Woodworking knives
Timken 17-22	0.90	0.45 C, 0.45 Mn, 1.25 Cr, 0.75 Si, 0.30 V, bal. Fe	Timken Steel & Tube Co.	Forgings, high temp. bolts
Timken 4-6% Cr W	0.75-1.25	0.15 Max C, 0.50 Max Mn, 0.50 Max Si, 4-6 Cr, bal. Fe	Timken Steel & Tube Co.	Machinery parts, still tubes, oil refinery tubing
Tungsten Magnet	5.25-5.75	0.65-0.76 C, 0.15-0.25 Si, bal. Fe	Vanadium-Alloys Steel Co.	Permanent magnets
Tungsten Magnet	5	0.70 C, 0.50 Cr, bal. Fe	Ludlum Steel Company	Magnets
Tungsten Magnet M5		C, W, bal. Fe	Halcomb Steel Company	Permanent magnets
Tungsten Magnet M6		C, W, bal. Fe	Halcomb Steel Company	Permanent magnets
U.S.S. 5W		C, 5 Cr, W, bal. Fe	Carnegie-Ill. Steel Corp.	Corrosion resistant parts
U.S.S. 12W		0.12 Max C, 12 Cr, W, bal. Fe	Carnegie-Ill. Steel Corp.	Corrosion resistant parts

Name	Wolfram	Composition	Reference	Uses
U.S.S. 17-W		0.12 Max C, 17 Cr, W, bal. Fe	Carnegie-Illinois Steel Corp.	Corrosion and heat resistant parts
United Magnet	0.60	0.6–0.9 C, 0 25–0.55 Mn, 0.25-2.1 Cr, bal. Fe	United Alloy Steel Corp.	Magnets, electrical machinery
Valve Steel Tungsten	14	3 Cr, 0.6 C, bal. Fe	Campbell "A List of Alloys" A.S.T.M. Proceedings Vol. 30 Part 1 (1930)	Valves
Valve Steel Very Hard	60	26 Fe, 5 Ti, 4 Cr, 3 C, 2 Ce	Campbell "A List of Alloys" A.S.T.M. Proceedings Vol. 30 Part 1 (1930)	Valves
M. P. Fould	0.10–0.15	less than 0.50% C, 0.200–0.600 Mn, 0.200-0.600% Si, less than 0.020 P, less than 0.015 S, 0.300 to 0.600 Cu	U. S. Patent 1,977,182 (Oct. 16, 1934)	Forgings and castings
K. Lowenstein W. Muller	32	*Medium Hard Alloy·* 55 Fe, 8 A, 4 Co, 1 C	U. S. Patent 1,847,617 (March 1, 1932)	Projectile, projectile casings, mines, torpedoes, cutting & drilling tools
	65	*Very Hard Alloy:* 10 Fe, 16 Cr, 7 Co, 2 C (Up to 25% of W. may be replaced by Mo. and up to 50% Co by Ni)		
J. Novak & R. Kresselring	5-6	20–30 Cr, 6–10 Ni, 10–15 Cu, 2.5–3% Carbide C	U. S. Patent 1,890,548 (December 13, 1932)	Rustproof seamless tubes
J. Novak & R. Kesselring	0.01–0.05	0.01–1 Cr, 0.25–0.5 Cu, 0.04–0.25 Ni, 0.03–0.1 C, below 0.005 P, below 0.04% S	U. S. Patent 1,876,467 (Sept. 6, 1932)	Boiler tubes, flues, stove or furnace parts, ship plates
W. Rohn	3	60 Ni, 15 Cr, 15 Fe, 3 Mo, 3 Co, less than 5% C	U. S. Patent 1,736,053 (November 19, 1929)	Surgical instruments, dentures injection cannulae
W. Rohn	3–8	Up to 25% Fe, 0.3–3 Be, 10–20 Cr, 2–5 Mo, 1–5 Co, bal. Ni	U. S. Patent 1,942,150 (January 2, 1934)	Surgical needles

The following is a supplementary list of some of the commercial ferrous tungsten alloys, other than those tungsten tool steels already described[12]:

Name	Tungsten	Composition	Reference	Uses
Agile Silver A-C Electrode	1.5	0.9 C, 0.7 Mn, 0.7 Cr, bal. Fe	American Agile Corp.	Welding electrode. Deposit should be heat treated
Agile Silver Black	8	0.6 C, 12 Cr, 8 Mo, 1.5 B, bal. Fe	American Agile Corp.	For welding high speed steel cutters. High speed steel
Agile Silver Chisel Electrode	1.5	0.8–1.0 C, 1.0 Si, 0.3–0.5 B, bal. Fe	American Agile Corp.	Welding electrode for chisels and shock resisting tools. Tough, shock resisting
Amotun	1.5	0.85 C, 4 Cr, 6 Co, 1.75 V, 8 Mo, bal. Fe	Atlantic Steel Co.	Cutting tools. High speed steel
Ark	1.5	0.81 C, 3.6 Cr, 7.9 Mo, 1 V, bal. Fe	Wm. Jessop & Sons Inc.	Tools, cutters. High speed steel
Atlantic V	18.5	0.8 C, 4.25 Cr, 2 V, 0.65 Mo, bal. Fe	Atlantic Steel Co. of America	Cutting tools. High speed steel

Name	Tungsten	Composition	Reference	Uses
Atlas XXX	3.75	1.35 C, bal. Fe	Canadian Atlas Steels Ltd.	Tools. Maximum wear resistance
Atlas A	9	0.30 C, 3.5 Cr, 0.45 V, bal. Fe	Ludlum Steel Co.	Hot work tools, piercers, punchers, die. Hot work steel
Atsil	0.5	0.5 C, 0.6 Mn, 0.3 Mo, 1.3 Si, bal. Fe	Atlantic Steel Co. of America	Shear blades, rivet sets, cutting tools. Shock resisting
Bethlehem Extra Special	14	C, 4 Cr, 2 V, bal. Fe	Bethlehem Steel Co.	Tools, cutters. High speed steel
Bethlehem No. 57 Special Hot Work	14	0.4 C, 3.5 Cr, 0.3 V, bal. Fe	Bethlehem Steel Co.	Spike cutters, hot headers, punches. Hot work steel
Bethlehem Moco	5.25	0.8 C, 5 Mo, 2 V, 4 Cr, 5.25 Co, bal. Fe	Bethlehem Steel Co.	Cutting tools, taps, reamers. High speed steel
Bethlehem 66 High Speed	5.6	0.81 C, 4.6 Mo, 1.6 V, bal. Fe	Bethlehem Steel Co.	Tools, cutters, taps, reamers. High speed steel
Bethlehem Mokut		W, C, Mo, Cr, bal. Fe	Bethlehem Steel Co.	Tools, cutters. High speed steel
C.H.W.	15.0	0.5 C, 2.75 Cr, V, bal. Fe	Latrobe Electric Steel Co.	Dies, punches, shear blades, trimmers. Hot work steel
C.L.W.	9.25	0.30 C, 3.25 Cr, 0.5 V, bal. Fe	Latrobe Electric Steel Co.	Extrusion and trimming dies, punches, shears. Hot work steel
Carpenter Permanent Magnet Type E	5.5	0.60 C, 0.20 Cr, bal. Fe	Carpenter Steel Co.	Magnetic units. Permanent magnet
Carpenter Permanent Magnetic Type G	3.75	0.90 C, 5.75 Cr, 36 Co, bal. Fe	Carpenter Steel Co.	Magnetic units. Permanent magnet
Carpenter Permanent Magnet Type F	8.75	0.80 C, 2.75 Cr, 0.2 Mo, 17.5 Co, bal. Fe	Carpenter Steel Co.	Magnetic units. Permanent magnet
Celero	2.75	1.35 C, 0.25 Cr, bal. Fe	Disston & Sons Inc.	Finishing tools.
Co Major		C, W, Cr, V, Co, bal. Fe	Jessop Steel Co.	Tools, cutters. High speed steel
Co-Mo	1.5	0.7 C, 9 Mo, 4 Cr, 1 V, 5 Co, bal. Fe	Braeburn Alloy Steel Co.	Tools, cutters. High speed steel
Cobaflux Magnet A	4	0.7 C, 5 Cr, 37 Co, bal. Fe	Bethlehem Steel Co.	Permanent magnets
Cobalt Magnet 37%	2.25	0.90 C, 4.25 Cr, 38 Co, bal. Fe	Latrobe Electric Steel Co.	Electrical equipment. Magnet steel
Columbia Special Wire Drawing	10.5	2.3 C, 1.85 Cr, bal. Fe	Columbia Tool Steel Co.	Wire drawing dies. Used unhardened
Congo	4	0.8 C, 4 Cr, 1.5 V, 5 Mo,14 Co, bal. Fe	Braeburn Alloy Steel Co.	Tools, cutters. High speed steel
Coppco 200	0.5	0.9 C,1.15 Mn, 0.5 Cr, bal. Fe	Copperweld Steel Co.	Tools, dies. Non-deforming oil hardening
Coppco Cro-Tung	2.5	0.5 C, 1.4 Cr, bal. Fe	Copperweld Steel Co.	Punches, chisels, tools. Tough
Creston No. 6		C, Mn, Cr, W, Mo, Ni, bal. Fe	Amalgamated Steel Co.	
Creston No. 7		C, Mn, Cr, W, Mo, Ni, bal. Fe	Amalgamated Steel Co.	
Crobalt		C, W, Co, Cr, bal. Fe	Michigan Tool Co.	Cutters. Cast alloy
D6-CO	18	0.8 C, 4 Cr, 6 Co, 1.75 V, bal. Fe	Disston & Sons Inc.	Tools, cutters. High speed steel
D.T.D. 49b	2–3	0.35–0.45 C, 1.0–1.75 Si, 0.5–1.0 Mn, 12.5–14.5 Cr, 12.5–14.5 Ni, bal. Fe		Aircraft valves. Austenitic

Name	Tungsten	Composition	Reference	Uses
Darwin 19		C, Co, W, Cr, bal. Fe	Darwin & Milner Inc.	Tools, cutters, reamers. High speed steel
Delloy G-P		C, W, Cr, V, bal. Fe	Delloy Metals	Cutters, tools. High speed steel
Denavis		C, W, Cr, bal. Fe	Denman & Davis	Tools, cutters, reamers. High speed steel
Diamond A	11.5	2.2 C, 0.4 V, bal. Fe	Midvale Co.	Dies. Air hardening
Disston 66	6	C, 6 Mo, 4 Cr, 1 V, 2 Cu, bal. Fe	Disston & Sons	Cutting tools. High speed steel
Disston 6-N-6	6	0.8 C, 4 Cr, 1 V, 6 Mo, bal. Fe	Disston & Sons	Cutting tools. High speed steel
Doquat		Fe-W		Cutting tools. Hard sintered alloy
Double Special	3.5	C, 0.25 Cr, 0.30 Mn, 0.45 Si, bal. Fe	Hawkridge Bros.	Burnishing tools. Water hardening
Dreadnaught	18	C, 4 Cr, 1.15 V, bal. Fe	Hawkridge Bros.	Tools, cutters, hacksaw blades. High speed steel
Durco D-10		Ni-Cr-Mo, W, Mn, Si, C Fe	Duriron Co. Inc.	Heat and corrosion resistant parts. Non-magnetic
Durex Iron		C, W, Mo, Cr, V, bal. Fe	Moraine Products Co. Div. General Motors Corp.	Bearings. Sintered
Durodie	2.5	0.4 C, 3.5 Cr, 0.5 V, bal. Fe	Wm. Jessop & Sons Inc.	Bolt dies, hot extrusion dies. Hot work steel
Dycast	1.25	0.35 C, 0.95 Si, 5 Cr, 1.25 Mo, bal. Fe	Latrobe Electric Steel Co.	Die casting dies
Dymal OH	0.5	0.90 C, 1.6 Mn, 0.5 Cr, 0.2–0.3 V, bal. Fe	Amalgamated Steel Co.	
E.I.S. 73	10	0.30 C, 3.5 Cr, 0.35 V, bal. Fe	Heppenstall Co.	Hot work dies. Oil or air hardening
Electrite CO-6	5.5	0.88 C, 4 Cr, 1.75 V, 4.5 Mo, 9 Co, bal. Fe	Latrobe Electric Steel Co.	Tools, cutters. High speed steel
Electric Locomo	2	0.8 C, 4 Cr, 5 Co, 1.25 V, 8.5 Mo, bal. Fe	Latrobe Electric Steel Co.	Hobs, saw teeth, lathe centers. High speed steel
Epco-Oil Hard	0.5	1.0 C, 0.5 Cr, 1.0 Mn, bal. Fe	Williamson Bros. Inc.	Dies, gauges, master tools
Eureka		C, Cr, W, V, bal. Fe	Welding Equipment & Supply Co.	High speed steel welding electrode
Extra Special Alloy		C, W, bal. Fe	Latrobe Electric Steel Co.	Tools
Fagersta AD 95	1.0	0.70 C, 0.25 Cr, 0.15 V, bal. Fe	Swedish Steel Mills	Coining die
Fagersta Brilliant WW	18	0.70 C, 4.5 Cr, 1.5 V, bal. Fe	Achorn Steel Co.	Tools, cutters. High speed steel
Fagersta Non-Deforming	0.45	0.95 C, 0.45 Cr, 1.05 Mn, bal. Fe	Achorn Steel Co.	Tools dies. Non-deforming
Fast Finishing	3.5–5.0	1.25–1.35 C, bal. Fe	Milne & Co.	Tools
Fisco 66	5.5	0.8 C, 4 Cr, 1.5 V, 5 Mo, bal. Fe	Faitoute Iron & Steel Co.	Tools, cutters. High speed steel
Fisco Cobalt	18.8	0.74 C, 4.5 Cr, 1.4 V, 0.6 Mo, 5 Co, bal. Fe	Faitoute Iron & Steel Co.	Tools, cutters, dies. High speed steel
Fisco Excell	18	0.8 C, 4 Cr, 2 V, 0.7 Mo, bal. Fe	Faitoute Iron & Steel Co.	Tools, cutters. High speed steel
Fisco High Speed	18	0.7 C, 4 Cr, 1 V, bal. Fe	Faitoute Iron & Steel Co.	Tools, cutters. High speed steel
Fisco Moly		C, W, Cr, V, Mo, bal. Fe	Faitoute Iron & Steel Co.	Tools, cutters. High speed steel

Name	Tungsten	Composition	Reference	Uses
Fisco Superior	20	0.8 C, 12 Co, 4 Cr, 1 V, 0.6 Mo, bal. Fe	Faitoute Iron & Steel Co.	Tools, cutters. High speed steel
Fisco Tiger	18	1.0 C, 4 Cr, 2 V, bal. Fe	Faitoute Iron & Steel Co.	Tools, cutters. High speed steel
Five Star	18	0.85 C, 4 Cr, 10.5 Co, 0.55 Mo, bal. Fe	Midvale Co.	Tools, cutters. High speed steel
Frasse Grade H	1.25–1.75	1.0-1.1 C, bal. Fe	Peter A. Frasse Inc.	Cutters, tools
G.D.H. Bronze Label	0.4–0.5	0.90–0.95 C, 1.0-1.1 Mn, 0.4-0.5 Cr, bal. Fe	Grammar, Dempsey & Hudson Co.	Tools, gauges, broaches, taps. Oil hardening
G.D.H. No. 212	0.9-1.2	0.45-0.50 C, 0.85-1.05 Cr, 0.15-0.25 Mo, bal. Fe	Grammar, Dempsey & Hudson Co.	Chisels, shear blades, die blocks
G.D.H. No. 350	3.5-3.7	1.25–1.35 C, bal. Fe	Grammar, Dempsey & Co.	Drills, dies, gear cutters, taps
G.D.H. Red Label	18–20	0.65–0.75 C, 3–4 Cr, 1-1.5 V, bal. Fe	Grammar, Dempsey & Hudson Co.	Tools, cutters. High speed steel
Gorham Imperial		C, Co, W, bal. Fe	Gorham Tool Co.	Tool bits, cutters. For heavy cuts
Gorham Imperial 9		C, 8-9 Mo, 8-9 Co, bal. Fe	Gorham Tool Co.	Tools, cutters
Gorham Molybdenum		C, W, Mo, Cr, V, bal. Fe	Gorham Tool Co.	Tools, cutters. High speed steel
Gormet		C, Cr, Co, Mo, W, bal. Fe	Gorham Tool Co	Cutters for iron, brass and bakelite. Cast mixture
Graph-Tung	2.8	1.5 C, 0.4 Mn, 0.65 Si, 0.5 Mo, bal. Fe	Timken Steel & Tube Co.	Blanking and drawing dies, coining dies, shear blades. Abrasion resistant graphitic steel
Gripmore Tool	1.0	0.95 C, 3.5 Cr, bal. Fe	Bisset Steel Co.	Hot work tools. Hot steel
H M-Blue Chip		C, W, Cr, V, bal. Fe	Firth Sterling Steel Co.	Tools, cutters. High speed steel
2B (HC)	11.25	0.48 C, 2.75 Cr, 0.3 V, bal. Fe	Jessop Steel Co.	Piercing punches, mandrels, grippers, heading dies. Hot work steel
H & R No. 1	17.75–18.85	0.55–0.75 C, 3.8-4.3 Cr, 0.90-1.25 V, bal. Fe	Houghton & Richards Inc.	Lathes and planer tools, cutters. High speed steel
H & R No. 2	18–19	0.80-0.85 C, 4.0-4.5 Cr, 2.0-2.25 V, 0.6–0.8 Mo, bal. Fe	Houghton & Richards Inc.	Lathe tools, drills, taps, reamers. High speed steel
H & R No. 4	18.5	0.8 C, 4.5 Cr, 1.75 V, 7.5 Co, 0.8 Mo, bal. Fe	Houghton & Richards Inc.	Cutters
H & R No. 7	5.5	1.3 C, 4.5 Cr, 4.5 Mo, 4 V, bal. Fe	Houghton & Richards Inc.	Broaches, reamers, chasers. High speed steel
H & R No. 15	15.5	0.37 C, 3 Mo, 4 Cr, 2 Ni, bal. Fe	Houghton & Richards Inc.	Extrusion dies, hot piercing punches. Hot work steel
H & R No. 57	5.75	0.8 C, 3.75 Cr, 4.5 Mo, 1.5 V, bal. Fe	Houghton & Richards Inc.	Taps, chasers, broaches, reamers
H & R No. 225	2.5	0.5 C, 1.5 Cr, 0.25 V, bal. Fe	Houghton & Richards Inc.	Dies, shear blades, cutters
H & R Cobalt High Speed Steel	18	0.75–0.80 C, 4 Cr, 5 Co, 1 V, bal. Fe	Houghton & Richards Inc.	Cutting tools. High speed steel
H & R Hot Works	10–11.5	0.30–0.35 C, 3–3.5 Cr, 0.3-0.5 V, bal. Fe	Houghton & Richards Inc.	Extrusion and swedging dies, shear blades. Hot work steel

Name	Tungsten	Composition	Reference	Uses
H & R Hot Work No. 2	9.25	0.33 C, 3.5 Cr, 0.5 V, bal. Fe	Houghton & Richards Inc.	Die casting dies, extrusion dies. Hot work steel
H & R Hot Works No. 6	1.35	0.35 C, 1.0 Si, 5 Cr, 1.75 Mo, bal. Fe	Houghton & Richards Inc.	Extrusion dies, piercing mandrels. Hot work steel
No. 3074 Hot Work	8–10	0.40–0.45 C, 2.5 Cr, 0.10–0.15 V, bal. Fe	Milne & Co.	Hot work tools and dies. Hot work steel
H & R Super Cobalt	20 21	0.8 C, 4–4.5 Cr, 1.3 V, 12 Co, 0.6 Mo, bal. Fe	Houghton & Richards Inc.	Cutters, hobs, millers. High speed steel
H & R Tungsten Oil Hardening	0.5	0.9 C, 1.1 Mn, 0.2 V, 0.5 Cr, bal. Fe	Houghton & Richards Inc.	Hobs, reamers, broaches, gauges
H.P.S.		C, W, Cr, V, bal. Fe	Poldi Steel Works	Hot work tools and dies. Hot work steel
H.W.D.	1.15	0.4 C, 5 Cr, 0.15 V, 1.5 Mo, 0.8 Si, bal. Fe	Firth-Sterling Steel Co.	Hot punches and dies. Hot work steel. Tough
Hard Facing Rod No. 217		C, Cr, Mn, W, Mo, bal. Fe	American Manganese Steel Div. American Brake Shoe Co.	Hard facing welding rod. Abrasion resistant
Hardrock 33	18	7 Co, 4 Cr, 1 V, C, bal. Fe	Industries Trading Co.	Tool bits. High speed steel
Hardsteel No. 2	1.6	47 Co, 26.8 Cr, 0.7 Mo, trace B, 2.7 Ni, 0.4 V, 2 Fe	Black Drill Co.	Hard drills
Hawk Prefak	0.5	0.90 C, 0.5 Cr, 1.25 Mn, bal. Fe	Hawkridge Bros.	Tools, cutters, dies. Non-deforming
Haynes Stellite No. 2400	17.5	2.3 C, 0.7 Mn, 0.5 Si, 31.3 Cr, 40 Co, 0.2 B, 0.3 Mo, 2.4 V, 4.2 Fe	Haynes-Stellite Co.	Cutting tools
HIA		C-Si-Cr-W-Ni, bal. Fe	Ludlum Steel Co.	Tools
Hidalgo RL	5.5	1.25 C, 0.4–0.5 Cr, bal. Fe	Hidalgo Steel Co.	Cutting tools. For finishing cuts on hard material
Hockleisteungstahl	2	10 Cr. 0.5 V, 1.5 C, 1.2 Si, 0.4 Mn, bal. Fe		Shear blades, dies
Hofors-46	0.5	0.90 C, 1.15 Mn, 0.5 Cr, 0.1 V, bal. Fe	Hofors Steel Works	Blanking dies, broaches, form tools, punches, taps
Hofors-711	2.5	0.50 C, 0.70 Si, 1.15 Cr, 0.15 V, bal. Fe	Hofors Steel Works	Broaches, milling cutters, blanking and heading dies
HSC No. 33	1.2	0.3–0.35 C, 0.9 Si, 5 Cr, 1.5 Mo, bal. Fe	Hoyland Steel Co.	Hot work tools. Hot work steel
HSC No. 350	3.5	1.25–1.35 C, bal. Fe	Hoyland Steel Co.	Tools. Fast finishing
H.V. Blue Chip	18	0.82 C, 4 Cr, 2 V, bal. Fe	Firth-Sterling Steel Co.	Finishing tools and cutters. High speed steel
HV-6	5.75	1.15 C, 0.3 Si, 4 Cr, 3 V, 5.25 Mo, bal. Fe	Latrobe Electric Steel Co.	Tools, cutters. High speed steel
Illium R		58 Ni, 21–23 Cr, W, 0–4 Cu, 4–6 Mo, Mn, bal. Fe	Burgess-Parr Co.	Chemical equipment, kettles, spray nozzles. Resist strong acids
Imperial Major	21–22	4–5 Cr, 13 Co, 1.5 V, 0.5 Mo, bal. Fe	Milne & Co.	Tools, cutters. High speed steel
Ingersolls DBL		C, W, Mo, Cr, bal. Fe	Ingersoll Steel & Disc. Co.	Tools, cutters. High speed steel
J.P.S. Steel	1.1–1.3	0.90–1.0 C, 0.45–0.60 Cr, bal. Fe	Wm. Jessop & Sons Inc.	Shock tools, threading, taps, reamers, broaches. Oil hardening
JBR Alloy		C, 6 Co, W, Cr, V, bal. Fe	Rennie Tool Co.	Tools, cutters. Tipped tools

Name	Tungsten	Composition	Reference	Uses
Ludlum DBL	4.8–5.5	0.75–0.80 C, 0.5–0.8 Si, 3.7–4.2 Cr, 1.5 V, 3.5–4 Mo, bal. Fe	Allegheny-Ludlum Steel Co.	Tools, cutters
Ludlum ML	18	C, 4 Cr, 2 V, 0.75 Mo, bal. Fe	Allegheny-Ludlum Steel Co.	Tools, cutters. High speed steel
M. G. R.	1.25	0.55 C, 1 Si, 0.3 Mn, 5 Cr, 1.25 Mo, bal. Fe	Latrobe Electric Steel Co.	Hot work tools and dies Hot work steel
M-M-1	1.25–2.25	0.65–0.85 C, 7.5–9.5 Mo, 3.5–4.5 Cr, 0.9–1.5 V, bal. Fe	Milne & Co.	Tools, cutters. High speed steel
Macco Radio	6	0.8 C, 4 Cr, 5.5 Mo, 1.8 V, bal. Fe	P. F. McDonald & Sons	Tools, cutters. High speed steel
Macco Superior High Speed	18.5	0.72 C, 4 Cr, 1 V, bal. Fe	P. F. McDonald & Sons	Tools, cutters. High speed steel
Maccomax		C, Cr, V, W, bal. Fe	P. F. McDonald & Sons	Tools, cutters. High speed steel
Malax AA	19	C, 4.25 Cr, 2 V, bal. Fe	Amalgamated Steel Co.	Tools, cutters. High speed steel
Malax AAA	19	C, 4.25 Cr, 2 V, 5–8 Co, 0.8 Mo, bal. Fe	Amalgamated Steel Co.	Tools, cutters. High speed steel
Mangano Special	0.50	0.90 C, 0.50 Cr, 1.20 Mn, bal. Fe	Latrobe Electric Steel Co.	Reamers, dies, threading taps trimming dies. Non-deforming
Maxtack	10	2.25 C, 2 Cr, 2.5 Mn, 1.0 Si, bal. Fe	Milne & Co.	Tools, cutters
2 B (MC)	13.5	0.35 C, 3 Cr, 0.25 Mn, 0.3 V, bal. Fe	Jessop Steel Co.	Tools. Tough
Jessco B		C, Co, W, Cr, V, bal. Fe	Jessop Steel Co.	Tools, cutters. High speed steel
Jessco A		C, W, Cr, V, bal. Fe	Jessop Steel Co.	Tools, cutters. High speed steel
K.D. 16	16	C, 4.5 Cr, 10 Co, 2.2 V, 1.5 Mo, bal. Fe	Hidalgo Steel Co.	Tools, cutters. High speed steel
Ketos	0.50	0.90 C, 0.50 Cr, 1.25 Mn, bal. Fe	Hawkridge Bros.	Blanking, trimming, and forming dies
KL	7.5	0.35 C, 7.5 Cr, 0.6 Mn, 1.5 Si, bal. Fe	Universal-Cyclops Steel Co.	Hot work dies. Resists abrasion and heat checking
K.M.	7.5	0.45 C, 7.5 Cr, 0.6 Mn, 1.5 Si, bal. Fe	Universal-Cyclops Steel Co.	Hot work dies. Resists abrasion and heat checking
KS	5.25	0.35 C, 5.25 Cr, 0.25 Mn, 0.20 V, 0.2 Mo, 0.9 Si, bal. Fe	Universal-Cyclops Steel Co.	Hot work dies. Hot work steel resists abrasion and heat checks
K.S. Magnet Steel	6–8	0.7–1.0 C, 1–2 Co, bal. Fe		Magnets, magnetos
Kut Kost		C, W, Cr, V, bal. Fe	General Tool & Die Co.	Tipped tools and cutters. High speed steel
Kut Kost Grade V		C, W-Co-1.5 B, bal. Fe	General Tool & Die Co.	Tools, cutters. For heavy cuts
Kut Kost Grade X		C, W-Co, 1.5 B, bal. Fe	General Tool & Die Co.	Tools, cutters. Centrifugally cast
Kut Kost Grade XV		C, W, Co, 1.5 B, bal. Fe	General Tool & Die Co.	Tools, cutters. Centrifugally cast
Kut Kost Grade XX		W, Co, 1.5 B, bal. Fe	General Tool & Die Co.	Tools, cutters. Light cuts
2B (LC)	10	0.30 C, 3.15 Cr, 0.3 V, bal. Fe	Jessop Steel Co.	Forming dies. Hot work steel
LCT	15	0.45 C, 3.0 Cr, 0.4 V, bal. Fe	Crucible Steel Co. of America	Hot swaging dies, extrusion dies, shear blades. Hot work steel

Name	Tungsten	Composition	Reference	Uses
LCT No. 2	11.5	0.45 C, 3 Cr, 0.4 V, bal. Fe	Crucible Steel Co. of America	Brass forging dies, punches, forming rolls. Hot work steel
Lehigh XXX High	18	0.7 C, 4 Cr, 1 V, bal. Fe	Lehigh Steel Co.	Lathe & planer tools, punches, reamers. High speed steel
Liberty	1.25	1.2 C, 0.3 Cr, bal. Fe	Hawkridge Bros.	Chaser and threading tools. Water hardening
LLCT	15	0.25 C, 4 Cr, 0.4 V, bal. Fe	Crucible Steel Co. of America	Piercing punches, extrusion dies. Hot work steel
Lockport Special	18	C, 4 Cr, 2 V, bal. Fe	Simonds Saw & Steel Co.	Tools, cutters. High speed steel
L.P.D.	1.4	0.30 C, 5 Cr, 1.75 Mo, 0.9 Si, bal. Fe	Latrobe Electric Steel Co.	Hot forging dies. Hot work steel
Mezzo Steel		C, W, Mo, Cr, V, bal. Fe	Cleveland Twist Drill Co.	Tools, cutters. High speed steel
Minerva Chisel	1.9–2.0	0.5 C, 1.75 Cr, 0.2 V, bal. Fe	Milne & Co.	Tools
Mo Chip Superior		C, Mo, Co, W, Cr, bal. Fe	Firth-Sterling Steel Co.	Tools, cutters
Mo Chip		C, Mo, Co, W, Cr, bal. Fe	Firth-Sterling Steel Co.	Tools, cutters
Mohican	1.5	0.8 C, 4 Cr, 1 V, 8.5 Mo, bal. Fe	Canadian Atlas Steels Ltd.	Tools, cutters. High speed steel
Morex		C, Mo, W, bal. Fe	Darwin's Ltd.	Tools, cutters. High speed steel
Nivarox		28 Ni, W, Mo, Be, bal. Fe	Heraeus-Vacuumschmelze A.-G.	Elinvar type
Non-Shrinkable Drill Rod	0.5	0.95 C, 1.2 Mn, 0 5 Cr, 0.2 V, bal. Fe	Anchor Drawn Steel Co.	Tools
Pure Ore Clipper		C-Cr-W-V, bal. Fe	Kloster Steel Co.	Cutters, tools. High speed steel
Pure Ore D-C-33		C-Cr-W-Si-Mo, bal. Fe	Kloster Steel Co.	Hammer dies, press tools. Hot work steel
Pure Ore D-C-66		C, W, Cr, bal. Fe	Kloster Steel Co.	Hammer dies, press tools. Hot work steel
Pure Ore Finishing Steel		C, W, bal. Fe	Kloster Steel Co.	Cutting tools. Wear resisting
Pure Ore Kapo		High C, high Cr, W, bal. Fe	Kloster Steel Co.	Dies, tools
Pure Ore Moly 6–6		C, W, Mo, Cr, V, bal. Fe	Kloster Steel Co.	Cutting tools. High speed steel
Pure Ore Prior		C, W, Cr, V, bal. Fe	Kloster Steel Co.	Cutting tools. High speed steel
Red Cut Cobalt B	18	0.78 C, 4 Cr, 6.75 Co, 1.86 V, 0.75 Mo, bal. Fe	Vanadium-Alloy Steel Colonial Steel Co.	Cutting and forming tools, reamers, taps. High speed steel
Red Star Tungsten Drill Rod	1.6	1.2 C, 0.7 Cr, 0.25 Mo, 0.2 V, bal. Fe	Anchor Drawn Steel Co.	Drill rod
Regin.711	2.5	0.5 C, 1.15 Cr, 0.2 V, bal. Fe	Uddeholm Co. of America Inc.	Shear blades, hot heading dies, chisels
Remalloy		12 Co, C, Cr, W, V, bal. Fe	Rennie Tool Co.	Tools, cutters. High speed steel
Rennite		12 Co, C, Cr, W, V, bal. Fe	Rennie Tool Co.	Tools, cutters. High speed steel
Rex MMM	5–6	0.85 C, 4 Cr, 1.6 V, 4–5 Mo, 5–5.5 Co, bal. Fe	Crucible Steel Co. of America	Cutters, tools, reamers, drills. High speed steel
Rex 1059	14	1.2 C, 4 Cr, 4 V, 0.75 Mo, bal. Fe	Crucible Steel Co. of America	Cutting tools, planer and shaper tools

Name	Tungsten	Composition	Reference	Uses
Rex 1092	5.5	4 Cr, 1.5 V, 3.75 Mo, bal. Fe	Crucible Steel Co. of America	Boring tools, broaches, chasers
SA Hy-Pro		C, Cr, V, W, Co, bal. Fe	Swedish American Steel Corp.	Cutting tools. High speed steel
SA N-N		C, W, bal. Fe	Swedish American Steel Corp.	Gripper dies, piercers. Hot work steel
Secoloy	17	2.5, C, 33 Cr, 44 Co, 2 Fe	Seaboard Steel Co. of America	Tool bits, cutters. Cast
Secovan	18	0.7 C, 4.5 Cr, 2.25 V, 0.65 Mo, bal. Fe	Seaboard Steel Co. of America	Tools, cutters. High speed steel
Semi High	1.1	1.1 C, 0.3 Cr, 0.2 V, bal. Fe	Disston & Sons Inc.	Tools. Semi-high speed
Seminole Hard	2	0.48 C, 1.3 Cr, 0.25 V, bal. Fe	Ludlum Steel Co.	Tools. Shock resistant
Seminole Medium	2	0.43 C, 1.3 Cr, 0.25 Mo, bal. Fe	Ludlum Steel Co.	Hot work tools and dies. Hot work steel
Seneca Hot Die	11	0.35 C, 3.5 Cr, 0.5 V, bal. Fe	Canadian Atlas Steels Ltd.	Punches, hot dies. Hot work steel
Silver Label	0.5	0.90 C, 0.5 Cr, 1.1 Mn, bal. Fe	Heller Bros. Co.	Hobs, taps, reamers, dies. Non-deforming
Simonds No 47	2	0.5 C, 1.4 Cr, 0.25 V, 0.25 Mo, 0.8 Si, bal. Fe	Simonds Saw & Steel Co.	Chisels. Shock resistant
Simonds O.H.D.	1.65	1.2 C, 0.6 Cr, 0.25 V, bal. Fe	Simonds Saw & Steel Co.	Punches, dies. Oil hardened
Simonds Red Streak	18	0.75 C, 4 Cr, 1 V, bal. Fe	Simonds Saw & Steel Co.	Drills, reamers, cutting tools. High speed steel
Simonds S.T.M.	1.6	0.8 C, 3.75 Cr, 1.1 V, 8.6 Mo, bal. Fe	Simonds Saw & Steel Co.	Cutting tools, drills, reamers. High speed steel
Simonds Super Cobalt	18	0.8 C, 4 Cr, 8 Co, 1.0 V, bal. Fe	Simonds Saw & Steel Co.	Cutting tools, drills, reamers. High speed steel
Simonds Teenax 46	0.50	0.9 C, 0.5 Cr, 1.15 Mn, 0.15 V, bal. Fe	Simonds Saw & Steel Co.	Taps, punches, dies
Simonds Tunco	18	0.7 C, 4 Cr, 5 Co, 1 V, bal. Fe	Simonds Saw & Steel Co.	Drills, reamers, cutting tools. High speed steel
Simonds Tungsten Magnet Steel		W-Fe	Simonds Saw & Steel Co.	Permanent magnet
Special		C, Cr, W, V, Mo, bal. Fe	Peninsular Steel Co.	
Special		C, Cr, W, V, bal. Fe	Bethlehem Steel Co.	Cutting tools. High speed steel
2002 Special		C, W, Cr, V, bal. Fe	Poldi Steel Works	
Special D		C, W, bal. Fe	Hidalgo Steel Co. Inc.	Tools
Special Wire Drawing Die	10.5	2 C, 1.8 Mn, 1.85 Cr, 0.5 Mo, bal. Fe	Columbia Tool Steel Co.	Drawing dies. For wire
Stag Mo		C, W, Cr, V, bal. Fe	Edgar Allen & Co.	Tools, cutters. High speed steel
Star Boron	1.5-2	0.5-0.6 C, 4-4.5 Cr, 1.5-2 V, 8-9 Mo, 7.75-.5 Co, 0.4-0.6 B, bal. Fe	Carpenter Steel Co.	Tools, cutters. High speed steel
Star-Max	1.5	0.78 C, 3.75 Cr, 1.15 V, 8.5 Mo, bal. Fe	Carpenter Steel Co.	Cutting tools. High speed steel
Star-Mo		C, Cr, Mo, W, V, bal. Fe	Firth-Sterling Steel Co.	Cutting tools. High speed steel
Stoodite K		Mo-W-Mn-Si, C-Fe	Stoody Co.	Hard facing alloy
Super	17.5	1.1 C, 3.75 Cr, 0.3 Mn, 3.25 V, 0.8 Mo, bal. Fe	Agawam Tool Co.	Lathe and planer tools. High speed steel

Name	Tungsten	Composition	Reference	Uses
Super DBL		C, W, Mo, Co, bal. Fe	Allegheny Ludlum Steel Co.	Tools, cutters. High speed steel
Super Star-Mo	5–6	0.80–0.88 C, 3.75–4.5 Cr, 1.7–1.9 V, 4–5 Mo, 8.5–9.5 Co, bal. Fe	Firth-Sterling Steel Co.	Tool bits. High speed steel
Superior Ark High Speed	18	0.70–0.75 C, 4 Cr, 1 V, bal. Fe	Jessop Steel Co.	Boring tools, threading dies, gear cutters. High speed steel
Suttonite		C, Cr, W, V, bal. Fe	Welding Equipment & Supply	High speed steel welding electrode
TCM	1.25	0.35 C, 5 Cr, 1–1.5 Mo, 1.0 Si, bal. Fe	Vulcan Crucible Steel Co.	Die casting dies. Hot work steel
T.T.Q. High Speed	22	0.73 C, 5 Cr, 11 Co, 1.6 V, bal. Fe	Wm. Jessop & Sons Inc.	Cutting tools for hard and abrasive material. High speed steel
Thermal BB	10–14	0.58 C, 3–4 Cr, 0.4 V, bal. Fe	Amalgamated Steel Co.	Tools, cutters. High speed steel
Toolweld 55		C, Cr, V, W, bal. Fe	Lincoln Electric Co.	Welding electrode for worn dies and tools. Shielded arc. High speed steel deposit
Toolweld 60		C, Cr, V, W, bal. Fe	Lincoln Electric Co.	Welding electrode for worn dies and tools. Shielded arc. High speed steel deposit
Torpedo	0.5	0.9 C, 0.5 Cr, 1.3 Mn, bal. Fe	Lehigh Steel Co.	Dies, punches, rivet sets. Non-deforming, oil hardening
Tuncro	2	0.50 C, 1.4 Cr, 0.25 V, bal. Fe	Atlantic Steel Co.	Chisels, punches, pneumatic tools, hot work dies. Hot work steel
Tungsten Hack Saw	1.0	1.2 C, 0.10 V, bal. Fe	Disston & Sons Inc.	Hack saws
Tungsten Hot Work	9	0.43 C, 2.5 Cr, 0.1 V, bal. Fe	Milne & Co.	Hot shearing, hot punches, hot drawing. Hot work steel
Two Star Special	18	0.80 C, 4 Cr, 2 V, 0.55 Mo, bal. Fe	Midvale Co.	Tools, cutters. High speed steel
Ultra Crystal Plus One		C, Cr, V, W, Co, bal. Fe	Adams & Osgood Steel Co.	Tools, cutters. High speed steel
USO-HE	1.6	1.5 C, 0.5 Cr, 0.25 V, bal. Fe	Hidalgo Steel Co. Inc.	Dies, gauges. Oil hardening, non-deforming
Uso Tungsten	18	4 Cr, 0.8 V, C, bal. Fe	Hidalgo Steel Co. Inc.	Lathe tools, drills, milling cutters. High speed steel
Uso 30 CF	8.8	0.30 C, 3 Cr, 0.25 V, bal. Fe	Hidalgo Steel Co. Inc.	Hot dies and tools. Hot work steel
"V" Moly High Speed	5.5	0.80 C, 4 Cr, 4.25 Mo, 1.5 V, bal. Fe	McInnes Co.	Tools, dies. High speed steel
Vanadium 6-6-2	5.75	0.8 C, 4.1 Cr, 1.6 V, 4.75 Mo, bal. Fe	Vanadium Alloys Steel Co.	Tools, cutters. High speed steel
Veribest Drill Rod	0.9	0.9 C, 1.1 Mn, 0.6 Cr, 0.24 V, bal. Fe	Diehl Steel Co.	Oil hardening drill rod.
Victory Cobalt	6	0.85 C, 5 Mo, 4 Cr, 2 V, 8.5 Co, bal. Fe	Vanadium Alloys Steel Co.	Cutting tools. High speed steel
Visto		C, Cr, V, W, bal. Fe	Hidalgo Steel Co. Inc.	Tools, cutters. High speed steel
Vulcan A-42		C, W, bal. Fe	Vulcan Crucible Steel Co.	Hot punches, die and pressure casting dies. Hot work steel

Name	Tungsten	Composition	Reference	Uses
Vulcan Blue Edge		C, W, Cr, bal. Fe	Vulcan Crucible Steel Co.	Pneumatic chisels, shear blades, cold rivet sets. Shock resisting
Vulcan Wolfram Cobalt	18	C, 4 Cr, 1 V, 4 Co, 0.5 Mo, bal. Fe	Vulcan Crucible Steel Co.	Cutting tools. High speed steel
W Tap		C, W, bal. Fe	Latrobe Electric Steel Co.	Tools
WT Drill Rod	1.27	1.23 C, 0.4 Cr, 0.3 V, bal. Fe	Latrobe Electric Steel Co.	Drill rod, tools
W.D.D.	3–6	C, bal. Fe	Latrobe Electric Steel Co.	Tools, dies. Hot work steel
W 2	16	0.17 C, 3.3 Cr, 0.8 V, 4 Co, 0.4 Ni, 0.6 Mo, bal. Fe		
Wire Drawing Alloy Special	10.5	2.35 C, 1.9 Cr, 1.65 Mn, 0.6 Si, bal. Fe	Columbia Tool Steel Co.	Tools, wire drawing dies. Abrasion resisting
Wizard	0.85	0.45 C, 0.8 Cr, bal. Fe	Agawam Tool Co.	Pneumatic chisels, shock tools
Wortle No. 4 Drawing Die	3.0	1.95 C, bal. Fe	Hawkridge Bros.	Drawing dies, tools
XL Chisel	2.1	0.53 C, 1.3 Cr, bal. Fe	Latrobe Electric Steel Co.	Chisels, punches. Oil hardening
Zip	17.5	0.65 C, 4 Cr, 7.5 Co, 1.65 V, 0.85 Mo, bal. Fe	Agawam Tool Co.	Lathe, planer and shaper tools. High speed steel

German Tungsten Tool and Special Steels During the War. The following is taken from an article by James P. Gill.*

(1) *Steels of the Poldi Hutte Works*

High Speed Steel

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co
MK Special	0.65	0.20	0.25	4.20	17.5	—	0.70	1.60	15.5
Poldi MK	0.65	0.20	0.25	4.20	17.5	—	0.70	1.60	9.50
Poldi MKH	0.78	0.20	0.25	4.20	17.5	—	0.70	1.60	9.50
Maximum Special 55	0.70	0.20	0.25	4.20	17.5	—	0.60	1.40	4.75
Maximum Special 55G-Radeco D	0.85	0.20	0.25	0.25	12.5	—	0.60	1.85	4.75
Maximum Special 30	0.70	0.20	0.25	0.25	17.5	—	0.60	1.40	2.50
Radeco K	1.35	0.20	0.25	1.05	17.5	—	—	1.35	5.25
Radeco-Radeco 2	1.30	0.20	0.25	5.00	10.75	—	—	4.20	—
Maximum Special G-Extra	0.85	0.20	0.25	4.20	9.75	—	—	2.40	—
Maximum Special	0.70	0.20	0.25	4.20	17.5	—	0.60	1.35	—
Maximum Special H	0.80	0.20	0.25	4.20	17.5	—	0.60	1.35	—
Maximum Special G-Maximum Special G3	0.82	0.20	0.25	4.20	7.75	—	—	2.00	—
Maximum Special MO	1.00	0.20	0.25	5.25	1.75	—	2.40	2.85	—
Maximum	0.70	0.25	0.25	4.00	17.5	—	0.60	0.50	—
000 Extra 6-Maximum P	0.75	0.25	0.25	4.00	16.85	—	0.40	0.35	—
Maximum G	0.75	0.25	0.25	5.00	8.50	—	0.55	0.80	—
00 Extra	0.75	0.25	0.25	4.00	15.75	—	0.50	0.15	—
000	0.65	0.25	0.30	5.00	10.25	—	0.40	0.10	—

---

* Gill, James P., "German Tool and Special Steels," *Iron Age*, 54A–54N (Sept. 13, 1945).

Chromium-Tungsten and Tungsten Steels

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co
301	0.32	0.35	0.30	2.25	9.50	—	—	0.25	2.40
KNO Extra	0.42	0.30	0.30	2.25	9.50	—	0.55	1.60	—
KNO	0.42	0.20	0.25	3.75	15.0	—	0.10	0.35	—
HPS	0.25	0.50	0.30	2.25	9.50	1.50	—	0.10	—
212	0.28	0.35	0.30	2.25	8.75	—	—	0.20	—
212 D2	0.30	0.35	0.30	2.75	4.35	—	—	0.55	—
425	0.30	0.35	1.10	1.45	3.75	—	—	—	—
425 D	0.32	0.35	1.10	2.45	1.90	—	—	0.35	—
Tenax NB	0.55	0.25	1.00	1.10	1.90	—	—	—	—
Tenax N-895	0.45	0.25	1.00	1.10	1.90	—	—	—	—
Tenax NF	0.35	0.25	1.00	1.10	1.90	—	—	—	—
0 Diamanthart	1.35	0.25	0.20	0.55	4.90	—	—	0.35	—
0 Diamanthart D	1.35	0.25	0.20	0.70	3.35	—	—	0.35	—
0 Extra	1.35	0.25	0.20	0.25	4.75	—	—	0.10	—
0 Extra D	1.35	0.25	0.20	0.25	3.35	—	—	0.20	—
Solar	1.20	0.50	0.25	1.60	1.45	—	—	0.15	—
SPS	1.20	0.30	0.20	0.40	1.15	—	—	—	—
SP	1.20	0.30	0.20	—	0.70	—	—	—	—
SST	1.00	0.30	0.20	—	1.15	—	—	—	—
Duplex Extra	1.05	0.35	0.25	0.25	1.15	—	—	0.20	—

Chromium Special Steels

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co
2002 Special	1.85	0.30	0.30	12.5	0.75	—	—	0.30	—

Tool Steels With Nickel

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co
CNB	0.38	0.50	0.25	1.50	0.60	4.25	0.30	—	—

Corrosion Resisting Steels

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co	Ti
L-ADVD	0.40	1.00	2.30	18.00	1.20	9.50	—	—	—	—

Heat Resisting Chromium Steels

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co	Ti
AKX, 12 Special	0.09	0.50	1.00	23.50	0.50	1.30	0.40	0.25	—	0.20

Corrosion Special Steels

Brand	C	Mn	Si	S	Cr	W	Ni	Mo	V	Cu	Ti
AKH	1.00	0.50	0.25	—	14.50	1.80	—	—	—	1.35	—

Corrosion Resisting Steels with Special Physical Properties

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Cu	Ti
AKR L-AKR	0.45	0.60	1.50	12.50	2.20	12.50	—	—	—	—
L-AKRD	0.45	0.75	1.50	15.00	2.30	13.00	—	—	—	—
AKRV	0.28	0.60	1.50	12.50	2.20	12.50	0.50	1.00	—	—
AKRVB	0.18	0.50	0.50	12.50	2.20	12.50	—	1.00	—	—
KAPTOR	0.35	0.60	1.50	12.50	2.60	12.50	—	1.25	—	—
KAPTOR D	0.35	16.00	0.40	13.50	3.20	—	—	—	—	—
AKS2	0.10	0.50	0.50	4.80	2.00	25.00	3.50	—	2.50	—

Chromium-Nickel Special Steels

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co
NIS2	0.36	0.60	1.90	1.70	0.50	2.20	—	—	—
TPE	0.28	0.40	0.25	1.50	0.50	3.00	0.30	—	—
Victrix Special 32 L-Victrix Special 32	0.26	0.50	0.25	0.75	0.65	3.40	0.30	—	—

Nickel and Tungsten Steels

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co
WO1	0.65	0.45	0.25	—	1.10	—	—	—	—
WO2	0.65	0.45	0.25	0.25	2.00	—	—	—	—
WO3	0.85	0.30	0.20	0.40	3.00	—	—	—	—
WO3 Special	0.85	0.60	0.30	0.50	3.25	—	0.35	0.15	—
WO3H Special	1.00	0.65	—	0.55	3.25	—	0.50	0.25	—

(2) *Steels of the Komotau Works*

Special Steels

Brand	C	Mn	Si	Cr	W	Ni	Mo	V	Co	Cu
Poldi Works Steels										
Extra F-GuB	1.70	0.40	0.40	18.00	1.25	1.40	—	—	—	—
Extra C3-GuB	1.90	0.40	0.40	18.00	1.25	1.40	—	—	2.75	—
ZR-GuB	2.10	0.40	0.40	21.00	1.75	1.00	—	0.40	—	—

(3) *Steels of the Edelstahlwerke Works*

High Speed Steels

Cobalt-Tungsten-Vanadium

	C	Cr	Mo	V	W	Co
Cobalt 11	0.80	4.25	0.65	2.23	12.50	5.00
Cobalt 111	0.80	4.25	0.65	2.25	12.50	2.75
Cobalt 111 N	0.80	4.25	0.65	2.00	10.00	2.50

Tungsten-Vanadium

	C	Cr	Mo	V	W	Co
SA 200	0.85	4.00	0.30	2.50	10 to 11	—
SA 500	1.35	4.25	0.30	4.30	10 to 11	—
SA 900	1.50	4.25	0.65	4.25	12.50	5.00
000 Special 31	0.80	4.00	0.30	2.60	10.00	—

Low Tungsten

	C	Cr	Mo	V	W
Rapid Spezial BN	0.80	4.00	0.30	1.60	8.00 to 10
Mo 325 X	0.90 to 10	4.00	2.50	2.50 to 3.00	2.20 to 2.50
Mo 1225 X	0.90 to 10	4.00	2.50	2.50 to 3.00	1.00 to 1.5

	C	Mn	Si	P	S	Cr	W	Ni	Mo	V	Co
AKRV-GuB	0.22	0.50	0.50	0.04	0.04	13.00	2.00	13.0	—	1.00	—
AKS2-GuB (Poldi Works Steels)	0.20	0.50	1.25	0.04	0.04	4.75	2.00	25.00	3.50	—	4.0

Low Tungsten Tool Steels

	C	Si	Mn	Cr	W
WSPS	0.75	0.35	0.35	0.30	0.70
WS P	1.20	0.25	0.30	0.15	1.00
TP	1.00	0.20	0.30	0.10	0.9 (-WSW)
MSA	0.80	0.30	0.30	—	0.60

General Purpose Steels

	C	Si	Mn	Cr	W
B MS	1.15	0.25	0.35	1.10	1.10

Steels for Use With Heat and Hydrogen

Steels for Medium High Temperature

	C	Si	Mn	Cr	Mo	Va	W
MC 1.11 V	0.20	0.30	0.40	2.50 to 2.75	0.40	0.80	0.40

For Very High Temperatures

Valve Steels

	C	Si	Mn	Ni	Cr	Va	W
GSE	0.45	1.50	0.70	13.00	15.00	—	1.25

(4) *Steels of the Krupp Works*

Tool Steels

	C	Si	Mn	P	S	Cr	Ni	Mo	V	W
Alloy Tool Steels										
BDF30............	0.30 0.36	0.80 1.00	0.25 0.35	0.025	0.02	0.90 1.10	—	—	0.15 0.20	1.70 2.00
BDF50............	0.40 0.46	0.80 1.00	0.25 0.35	0.025	0.02	0.90 1.10	—	—	—	1.70 2.00
BDF Spezial....... (brand)	0.54 0.60	0.80 1.00	0.85 1.00	0.025	0.02	—	—	—	—	1.70 2.00

Tool Steels

Brand	C	Si	Mn	P	S	Cr	Ni	Mo	V	Ti	W
NFKC.........	1.35 1.45	0.15 0.30	0.25 0.35	0.025	0.02	0.40 0.50	—	—	0.20 0.30	—	3.00 3.50
WA904.........	0.25 0.30	0.20 0.40	0.30 0.50	0.025	0.02	1.00 1.20	—	—	0.15 0.20	—	3.50 4.00
WA904.........	0.30 0.35	0.15 0.35	0.20 0.40	.025	0.02	2.20 2.50	—	—	0.60 0.65	—	4.00 4.50
WA Universal	0.40 0.45	0.50 0.70	0.30 0.50	0.025	0.02	1.20 1.50	—	0.40 0.50	0.75 0.85	—	0.40 0.50

Electrode Steels

Electrodes for Hard Surfacing

Brand	C	Si	Mn	P	S	Cr	Ni		Co	W
Zeus EA Zeus Ga Percit Extra.......	1.20 1.40	2.00 3.00	0.20 0.60	0.025	0.02	26.00 28.00	— Co	—	57.00 63.00	3.80 4.80
Zeus EA Zeus GA Percit Special......	1.40 1.60	1.30 1.60	0.20 0.60	0.025	0.02	25.00 30.00	30.00 35.00	— V	—	4.00 4.50
Zeus EA leg. NFKC......	1.35 1.45	0.15 0.30	0.25 0.35	0.025	0.02	0.40 0.50	 Mo	0.20 0.30	Ti	3.00 3.50
Zeus EA Zeus GA leg. K.M.........	0.92 0.98	0.30	0.30	0.025	0.02	3.50 4.00	2.20 2.50	2.70 3.00	0.10 0.15	1.20 1.50
Zeus EA Zeus GA leg. DFMV 5....	1.30 1.40	0.30	0.30	0.025	0.02	3.00 4.50	—	4.20 4.50	—	10.00 11.00

(5) *Steels of Leipzig Rochlingstahl G.M.B.H.;*

High Speed Steels

Brand	C	Mn	Si	Cr	Ni	W	Mo	V	Co
Gigant 66..............	1.40 1.50	0.20 0.30	0.20 0.30	4.00 4.50	— —	12.00 13.00	0.40 0.70	4.20 5.00	4.20 5.00
Gigant Uno.............	0.72 0.80	0.20 0.30	0.30 0.30	4.50 4.50	— —	13.00 13.00	0.70 0.70	1.50 1.80	5.00 5.00
Gigant 33..............	0.85 0.95	0.30 0.30	0.30 0.30	4.50 4.50	— —	13.00 13.00	0.70 0.70	2.00 2.30	2.30 2.60

Brand	C	Mn	Si	Cr	Ni	W	Mo	V	Co
Gigant N	0.72	0.30	0.30	4.50	—	13.00	0.70	1.50	2.30
	0.80	0.30	0.30	4.50	—	13.00	0.70	1.70	2.60
Gigant	1.05	0.30	0.30	4.50	—	11.00	0.40	2.30	—
	1.15	0.30	0.30	4.50	—	12.00	0.70	2.60	—
Kosmos	0.82	0.30	0.30	4.50	—	11.50	0.60	2.35	—
	0.90	0.30	0.30	4.50	—	12.50	0.80	2.65	—
RSV	0.72	0.30	0.30	4.50	—	12.50	0.80	1.80	—
	0.85	0.30	0.30	4.50	—	12.50	0.80	2.00	—
RSZ Special	0.75	0.30	0.30	4.50	—	10.50	0.60	1.30	—
	0.83	0.30	0.30	4.50	—	11.50	0.80	1.50	—
RSZ	0.72	0.30	0.30	4.50	—	11.50	0.40	0.80	—
	0.80	0.30	0.30	4.50	—	11.50	0.60	1.00	—

Tool Steels for Hot Work

Brand	C	Mn	Si	Cr	Ni	W	Mo	V	Co	Cu
RWS	0.33	0.20	0.25	3.25	—	2.60	—	0.25	—	—
	0.36	0.30	0.35	3.45	—	3.00	—	0.35	—	—
WNC	0.35	0.20	0.30	1.30	3.20	5.00	—	—	—	—
	0.40	0.30	0.40	1.50	3.60	5.50	—	—	—	—
RCW 2	0.24	0.20	0.20	2.20	—	9.00	—	—	—	—
	0.30	0.30	0.30	2.80	—	10.00	—	—	—	—
SGM 2	0.31	0.30	0.20	2.20	—	7.50	—	0.50	2.50	—
	0.35	0.30	0.30	2.80	—	8.50	—	0.50	2.50	—
SGM 4	0.24	0.30	0.30	1.30	—	5.00	0.50	—	4.50	1.20
	0.30	0.30	0.30	1.60	—	5.50	0.70	—	5.00	1.50
RWS 2	0.24	0.30	0.40	1.10	—	4.00	—	—	—	—
	0.28	0.30	0.50	1.20	—	4.50	—	—	—	—
RWS 4	0.32	0.40	0.80	1.30	—	4.00	0.40	—	—	—
	0.38	0.50	1.00	1.60	—	4.50	0.60	—	—	—
RCNW	0.33	0.30	0.20	1.30	4.00	0.90	—	—	—	—
	0.38	0.45	0.30	1.50	4.50	1.15	—	—	—	—
PWDN	0.25	0.30	0.30	0.60	4.50	3.80	0.65	—	—	—
	0.32	0.30	0.30	0.80	4.50	4.30	0.85	—	—	—

Tool Steels for Cold Work

Brand	C	Mn	Si	Cr	Ni	W	Mo	V	Co
RUS 4	0.95	0.40	0.20	1.40	—	0.90	—	—	—
	1.10	0.60	0.30	1.60	—	1.10	—	—	—
T 76	1.45	0.20	0.20	0.60	—	(7.0 max)	0.30	0.30	—
	1.55	0.30	0.30	0.80	—	7.80	—	0.50	—
RTW 3-Special	1.30	0.20	0.20	0.60	—	4.60	—	—	—
	1.40	0.30	0.30	0.80	—	5.00	—	—	—
RTW 1	1.15	0.20	0.15	0.10	—	1.10	—	—	—
	1.25	0.30	0.25	0.20	—	1.30	—	—	—
RTW 2	0.33	0.30	0.90	1.00	—	2.60	—	—	—
	0.40	0.40	1.10	1.20	—	3.00	—	—	—
Robust M	0.40	0.40	1.10	1.20	—	2.25	—	—	—
	0. 6	0.40	1.10	1.20	—	2.50	—	—	—
RTWK	0.60	0.20	0.20	1.00	—	2.20	—	0.10	—
	0.65	0.40	0.30	1.50	—	2.50	—	0.20	—
SKSV	0.65	0.23	max	—	—	0.50	—	0.10	—
	0.73	0.33	0.15	—	—	0.60	—	0.15	—

High Speed Steels

Brand	C	Mn	Si	Cr	Ni	W	Mo	V	Co
Gigant 11	0.92	0.20	0.20	3.50	—	1.20	2.20	2.20	—
	0.98	0.35	0.35	4.00	—	1.50	2.50	2.50	—
Gigant 22	0.78	0.20	0.20	3.50	—	7.30	—	1.80	—
	0.85	0.35	0.35	4.00	—	8.00	—	2.00	—
Gigant 44	1.30	0.35	0.35	4.00	—	9.00	—	3.50	—
	1.40	0.35	0.35	4.50	—	10.00	—	4.00	—
Gigant 5	0.87	0.35	0.35	3.50	—	9.00	—	1.90	2.50
	0.95	0.35	0.35	4.00	—	10.00	—	2.20	3.00

Tool Steels for Hot Work

Brand	C	Mn	Si	Cr	Ni	W	Mo	V	Co
RWA	0.25	0.20	0.15	2.20	—	4.00	—	0.50	—
	0.35	0.40	0.25	2.50	—	4.50	—	0.60	—
NGSA	0.40	0.30	0.50	1.20	—	0.40	0.40	0.75	—
	0.50	0.50	0.70	1.50	—	0.50	0.50	0.85	—

(6) *Steels of the Bohler Works*

High Speed Steels

Brand	C	W	V	Mo	Cr	Co
CC Special	0.75	18.00	1.60	0.80	4.00	19.00
CC	0.80	18.00	1.60	1.00	4.20	9.00
Super Rapid Extra 500	0.85	18.50	2.00	0.50	4.00	5.00
Super Rapid Extra 214	0.70	19.00	1.70	—	4.30	2.40
Super Rapid Extra HV	0.90	14.50	2.00	1.15	4.50	—
Super Rapid Extra	0.65	18.50	1.30	—	4.00	—
Super Rapid	0.65	15.50	0.60	—	3.75	—

Special Tool Steels

Brand	C	Si	Mn	Cr	W	V
RM Special Sehr Hart	1.50	0.25	0.25	0.65	7.50	0.40
Special Sehr Hart	1.40	0.25	0.25	0.65	4.75	0.25
Special Sehr Hart	1.30	0.25	0.25	0.65	4.75	0.25

Alloy Tool Steels

Brands	C	Si	Cr	W	V	Mn
KP	1.30	0.20	—	4.75	—	0.30
KL	0.50	0.85	1.60	1.90	0.10	0.45
MY Extra	0.40	0.90	1.00	1.85	—	0.35
Amutit	1.00	0.25	1.10	1.50	—	0.90
TWW	1.25	0.25	0.85	1.65	—	0.30
TW	1.15	0.25	—	0.90	—	0.30
SW	1.00	0.20	—	0.90	—	0.30
TWV	1.20	0.20	—	1.20	—	0.25

Tool Steels for Cold Works

Brand	C	Si	Mn	Cr	W	V	Mo	Ni
TWV	1.20	0.20	—	—	1.20	0.10	—	—
WON	0.80	0.30	0.35	—	—	0.35	—	—

Tool Steels for Hot Works

Brand	C	Si	Mn	Cr	W	V	Co	Mo	Ni
WPZ	0.30	0.30	0.30	2.25	9.00	0.35	2.25	—	—
WKZ	0.30	0.30	0.40	2.25	8.50	0.40	—	—	—
WPD	0.25	0.30	0.35	1.85	0.90	—	—	2.85	2.50

High Speed Steels

Available 1944

Brand	C	Si	Mn	W	Cr	Mo	V	Co
Super Rapid, Extra 214 A	0.70	0.30	0.30	9.50	3.70	—	2.80	2.80
Extra Rapid 300 A	1.20	0.30	0.30	10.50	4.30	—	3.80	—
Super Rapid, Extra HVA	0.90	0.30	0.30	9.50	3.80	—	2.50	—
Super Rapid, Extra A	0.65	0.30	0.30	8.50	3.80	—	1.80	—
MO Rapid Extra 3 A	1.00	0.30	0.30	1.35	3.80	2.35	2.35	—

Tool Steels

Brand	C	Si	Mn	W	Cr	Mo	V	Co	Ni
Special Sehr-hart A	1.40	0.25	0.25	3.25	0.65	—	0.25	—	—
WKV	0.45	0.60	0.25	0.50	1.35	0.50	0.90	—	—
WKZ 50	0.30	0.60	0.25	4.35	1.35	—	0.65	—	—
WM	0.30	0.30	0.30	3.85	1.05	—	0.20	—	—
WM 2	0.35	0.90	0.30	1.85	0.05	—	0.20	—	—
KR Special	2.10	0.35	0.30	0.70	12.00	—	—	—	—

"The study of the compositions reveals that there was a decided preference in 1939 for high speed steels containing about 13 per cent tungsten, about 4 per cent chromium and high vanadium content, the vanadium content being from 1.5 per cent to as high as 5 per cent. The carbon was likewise proportionately increased with the vanadium content, in one instance being as high as 1.50 per cent and a cobalt content of 4.75 per cent. Many of the high speed steels contained cobalt from as low as about 2 per cent to as high as 15 per cent. As a result of the lack of alloying metals a high speed steel was developed containing from 0.90 to 1.00 per cent carbon, about 4 per cent chromium and a tungsten molybdenum and vanadium content each within the limits from 2 to 3 per cent.

"All of the men interviewed who manufactured this steel were very enthusiastic regarding its performance. Dr. Houdremont stated that it averaged about 20 per cent better than a standard 18 per cent tungsten high speed steel for general applications. Molybdenum high speed steels did not seem to find much favor among either the German manufacturers or users, even though several of the companies had obtained licenses to manufacture high speed steel of the Momax type. Little or no molybdenum was produced in Germany or by its satellites, which may explain its small use. As a matter of fact it is significant that the entire German industry of tool and special steels did not take advantage of the properties molybdenum imparts to steel as have the American manufacturers."

Effect of Tungsten in Cast Iron. (Bulletin of the British Cast Iron Research Association, 1945). According to Campion, an iron containing 0.65 per cent combined carbon, 2.7 per cent graphite, 1.5 per cent silicon, and 0.5 per cent manganese, had a tensile strength of 11.8 tons per sq in which was increased to 17.9 tons by the addition of 1.2 per cent of tungsten. However, according to Piwowarsky, an iron containing 3.6 per cent total carbon, 2.6 per cent graphite, 1.1 per cent silicon and 0.9 per cent manganese, had a tensile strength of 14.6 tons per sq in. With an addition of

0.56 per cent of tungsten, the tensile strength became 15.9 tons, while with an addition of 1.16 per cent tungsten, the tensile strength was 17.3 tons.

III. NON-FERROUS ALLOYS

III. 1. **Stellite** (Co-Cr-W)[10]

Stellite (cobalt-chromium-tungsten alloy) as a cutting tool was first placed on the market in 1913 by Haynes, its inventor. When iron is added to it, the resultant alloy is termed "festel" metal.

The various "Haynes-Stellite" alloys retain a higher hardness above 1100° F than the best high-speed steel. A typical form of stellite has the following approximate analysis:

	Co(%)	Cr(%)	W(%)	C(%)
Stellite	35	33–35	10	1.5–2.0
J-Metal	45–55	30–35		12–17

The so-called "J-metal" and "2400" alloys are used for cutting tools and "Haynes-Stellite" Nos. 1, 12, and 6 for hard facing welding rod. Approximate compositions of the three hard facing rod alloys are:

	Co(%)	Cr(%)	W(%)
No. 1	>43	<34	<14
No. 12	>47	<34	<10
No. 6	>55	<33	<6

Mention may be made of the recent development of the Co-Cr-W alloys in the form of the "98-M-2" tools, which can machine steel at even higher cutting speeds than "J-Metal" or "2400" tools, with longer life between grinds. These 98-M-2 tools are instrumental today in making big increases in the production of shells, aircraft parts, gun parts, tank parts, armor plate and many other products vital to the war effort.

A photomicrograph of the Co-Cr-W alloys shows that their structure consists of complex chromium and tungsten carbides imbedded in a solid solution matrix, principally of cobalt.

Because the alloys possess good resistance to corrosion and great wear resistance, they find use in the following applications: valves or other equipment dealing with acids and other chemicals; hard facing of plowshares, excavating equipment, tractor treads, dies, hot shear blades; knives, punches, shears, billet scrapers, etc. for cutting hot metals. Stellite is also used for coating the exhaust valves of internal combustion engines, such as those used in aircraft, trucks and buses.

The extreme smoothness of polished cobalt-chromium-tungsten alloy surfaces renders the alloy valuable as a reflector and in the burnishing of other metals.

Haynes-Stellite No. 6 can stand several months of outdoor exposure without loss of reflectivity.

Alloys containing cobalt, chromium and tungsten have been used as oxy-acetylene welding rods.

Low chromium-tungsten steels have been used where strength at moderately elevated temperatures is desired, for instance, for armor plates, tools and magnets.

III. 2. **Tungsten-Molybdenum Alloys**

These alloys can be prepared either by thoroughly mixing the metal powders, pressing into bars and sintering, or by reducing the mixed oxides in hydrogen. Because of their higher resistance, the W-Mo alloys may be used instead of tungsten as heaters for indirectly heated cathodes in the thermionic valves.

Tungsten-molybdenum alloys have been used as substitutes for platinum in dentistry.

III. 3. **Nickel-Tungsten Alloys**

Ni-W alloys are prepared in the same way as W-Mo alloys, but have no particular industrial applications. However, they form the basis for a series of acid-resisting alloys. It is interesting to note that nickel's resistance to attack by a 65 per cent acid can be increased fourfold by the addition of 5 per cent tungsten and twelvefold by the addition of 10 per cent tungsten.

III. 4. **Tungsten-Cobalt Alloys**

These alloys can be prepared by fusion of bars made by sintering the mixed metal powders. Because of their age-hardening properties, the alloys are specially suitable for swaging dies for hot-working tungsten. The product, consisting of 80 per cent W, 16 per cent Co and 4 per cent C, is extremely hard and is used as substitute for diamond in oil-well drilling.

An age-hardening alloy containing 20 per cent tungsten and 30 per cent cobalt in a carbon-free iron-base is said to surpass the best grades of high-speed steel in metal-cutting service. It can be cast and hot-forged.

An alloy of tungsten with 2 to 10 per cent cobalt has been patented in Germany for breeches for naval guns.

III. 5. **Copper-Tungsten Alloys and Silver-Tungsten Alloys**

Compound contact metals, made by incorporating silver or copper with tungsten, are used as materials for switches, circuit breakers and other switch gear. These compound contacts do not weld or stick during operation; are hard and do not "pit" and have good electrical and heat conductivity. The life of a tungsten-copper contact in an oil circuit-breaker is 150,000 operations, that is about six times of an ordinary copper contact. They are made by the following methods[11]:

"Method I is basically different from the other two. The starting material, tungsten or molybdenum powder, is pressed into the desired shape and sintered; this process gives a body of the proper dimensions and porosity. The body is then in the form of a sponge, and the pores are filled by immersion in molten silver or copper.

"Method II is much different. The starting point here is a mixture of the two powdered metals, such as tungsten and silver. These mixed powders are pressed and pre-sintered at a relatively low temperature, after which the slug is machined into the final shape. It is then sintered at a higher temperature to give the correct properties.

"The processing steps in Method III are somewhat different. The starting material is the same as in Method II. The mixed powder is pressed, the pressure varying with the type of material, being usually between 40 and 80 tons per sq in. The compact is then sintered at a temperature proper for the basic material and the final application of the part. The definite form is then obtained by mechanical working, such as re-pressing, hammering, or extruding; these last steps are accomplished cold or hot."

Copper-tungsten alloys having a tensile strength of 175,000 psi, a Rockwell hardness of B-110, an electrical conductivity of 30 per cent, and a specific gravity of 14.5 g/cc have been made. A material of such high specific gravity, tensile strength, and electrical conductivity should find considerable industrial application, particularly in the aircraft, automotive, electrical, and instrument industries.

Elkonite, an alloy of copper and tungsten, is employed as lining for bearings, electrodes for spot welding, and as contacts for circuit breakers and switches. Cletaloy, another new type of copper-tungsten compound, is used for the same purposes. On account of their high density, copper-tungsten alloys find applications in radium therapy, providing adequate protection from the penetrating α-rays. As these alloys in thinner screens are as effective as the thicker screens of lead, the former are accordingly preferable in radium therapy.

III. 6. Tungsten-Nickel-Copper Alloys*

Smithells' "Heavy Metal" is one of the most interesting products of powder metallurgy. According to the patent U. S. 2,183,359, the com-

---

* Housner, Henry H., "Some Modified Heavy Metal Alloys", *Metals and Alloys*, 1335–1338 (Dec., 1943).

position of the alloy lies within a range of 3½ to 16½ Ni, 1½ to 13½ Cu and 83 to 95 per cent W. A special composition of Heavy Metal of 2 Cu, 5 Ni and 93 per cent W has been described by G. H. Price, C. J. Smithells and S. V. Williams. "The Heavy Metal", composed of tungsten, nickel and copper, "has a density of not less than 16 gr per cc and consists of large grains of tungsten cemented together by a copper-nickel-tungsten alloy, there being not more than 1500 grains of tungsten per square millimeter of section of the material. "The high densities of certain types of the material with 90 per cent W (or more) make these types valuable for being used as containers for radium. The radiation absorption coefficient of this type of high-density material is 30 to 40 per cent higher than the absorption coefficient of lead. Again, heavy metal and other tungsten-nickel-copper compound materials may be used to balance crankshafts of aeromotors, for balance weights on controllable-pitch airscrews or for the centrifugal clutchplates which provide the slipping mechanism for supercharger drives and the like.

Apart from these applications, tungsten-nickel-copper compounds may be used successfully in the rotors of gyroscopes and gyro-compasses where a concentrated mass, combining high strength and resistance to creep is required. For these purposes, a material with optimum qualities of density, of tensile strength and elongation has to be used. In fact a material with less density but better tensile strength and especially with high elongation is preferable for uses such as these.

Tungsten-nickel-copper compound materials may also be used for sparking contacts in air circuit breakers. Their ability to withstand material transfer, their relative good conductivity and high hardness permit the use of these materials, where high currents, like short circuit currents, may be expected and contact wear has to be avoided. Obviously in these applications high conductivity and hardness are more important than density."

III. 7. **Lead-Tungsten Alloys**

Lead and tungsten do not form solid solutions on freezing. But if a third metal, such as antimony, is incorporated, homogeneous alloys are formed. On account of their hardness and high density, such alloys have been used for making small arms ammunition and shot. U. S. Patent 1,703,577 gives the following compositions of such alloys:

Tungsten	0.02 to 3
Lead	47 to 80
Antimony	15.5 to 25
Copper	0.7 to 10
Tin	0.5 to 25

III. 8. Acid-Resisting Alloys

Alloys of nickel, chromium and tungsten are found to be highly resistant to concentrated mineral acids. An alloy containing 2 to 10 per cent tungsten has been developed under the name Contracid. For economic reasons, part of the nickel component in this alloy may be replaced by iron.

An alloy containing 20 per cent tungsten, 15 per cent chromium and 65 per cent cobalt, unaffected by organic acids or ordinary antispetics is used for cutting tools and for surgical instruments. A similar alloy known as Amaloy containing tungsten, chromium and nickel, is used for the same purposes.

III. 9. Miscellaneous Alloys

A British steel containing 13 per cent chromium, 13 per cent nickel, 3 per cent tungsten is used for anti-corrosion and heat resisting purposes.

Eatonite, a new long-wear valve facing alloy, is said to be the hardest valve facing material known to the industry. This new alloy containing chromium, nickel, tungsten and cobalt, will retain its hardness in the "red zone" (above 1000° F) and at the same time resist corrosion.

For use in tipping the nibs used in the cheaper grades of fountain pens, the following alloys have been proposed:

U. S. Patent 2,074,474 (1937)

	Per cent by weight
Ex. 1	
Tungsten	65
Cobalt	10
Palladium	20
Osmium	5
Ex. 2	
Tungsten	80
Cobalt	10
Palladium	8
Iridium	2
Ex. 3	
Tungsten	65
Cobalt	10
Palladium	15
Ruthendium	10

U. S. Patent 2,021,021 (1935)

	Per cent by weight
Platinum, ruthenium osmium	2 to 40
Tungsten	50 to 70
Cobalt and/or nickel	5 to 25
Boron and/or carbon and/or silicon	0.5 to 5

U. S. Patent 1,566,534 (1925)

	Per cent by weight
Tungsten	80 to 90
Platinum	10 to 17
Iridium	1 to 3

U. S. Patent 2,072,368
65 per cent W, 10 per cent Co, 20 per cent Pt and 5 per cent Os
U. S. Patent 2,072,676
65 per cent W, 10 per cent Co, 20 per cent Pt and 5 per cent Ru
U. S. Patent 2,074,474
65 per cent W, 20 per cent Pd, 10 per cent Co and 5 per cent Os

The "Heavy Alloy" of the British Electric Co.—a sintered copper-nickel-tungsten powder mixture pressed at 5 to 10 tons per sq in and heated to 1800° F—containing 90 per cent W, 7.5 per cent Ni 2.5 per cent Cu, is suitable for radium containers, circuit-breaker contacts and machine-balancing weights (British Patent 447,567; U. S. Patent 2,183,359). Other patents concerning the so-called "heavy metal" are U. S. Patent 1,315,859; 1,747,133; 2,183,359.

Poppet valves for internal combustion engines may be made by compacting iron, nickel, tungsten and chromium powders (U. S. Patent 1,359,353).

An alloy of 80 per cent tungsten and 20 per cent chromium has been used as a substitute for diamond in wire-drawing dies.

Aluminum hardened with a small amount of tungsten and containing copper, tin and antimony, called Partinum, is said to have been used in France for automobile construction. An alloy of aluminum, tungsten and copper is made into propeller blades.

An alloy containing 75 parts of gold, 10 to 15 parts of tungsten and 10 to 15 parts of nickel, may be used in jewelry as a substitute for platinum.

An alloy containing 90 per cent Ag and 10 per cent W is said to be used as electrical contact in airplanes.

A welding electrode, according to U. S. Patent 1,972,463, can be made by using metal powders derived from their carbonyls (such as iron, nickel, cobalt, tungsten and molybdenum) in combination with a fluxing agent such as borax, silicate, ammonium, chloride, fluorspar, silicic acid or boric acid.

U. S. Patent 2,004,259 discloses that valve seat can be made by using a compact comprising 80 per cent tungsten, 19.7 per cent copper and 0.3 per cent carbon.

Other uses are: in dentistry to replace platinum pins; and in chemistry to replace a number of platinum chemical apparatus; it is said that the addition of small amounts of tungsten improves the usefulness of spark plugs, phonograph needles, razor and knife blades.

Tungsten forms alloys with a number of metals but they are generally of little industrial importance. They are W-Al, W-Bi, W-Zn, W-Hg, W-Sn, W-Sb, W-Ti, W-Zr, W-Hf, W-Th, W-Va, W-Tl, etc. References to these and other alloys are given in Appendix IV.

The following is a list of some of the commercial non-ferrous tungsten alloys[12]:

Name	W	Composition Others	Manufacturer or Reference	Uses
Amaloy		Ni, Cr, W	"International Critical Tables," Vol. II, 1927	Corrosion- and heat-resistant parts
Amsco No. 217		Cr, Mo, W	American Manganese Steel Co.	Welding rod for hard surfacing
Arkit	16	38 Co, 30 Cr, 10 Ni, 4 Mo, 2.5 C	"Metal Industry Handbook," The Metal Industry Magazine, London, 1932	High-speed cutting tips of lathe tools
Bario, Hard	25	30 Co, 30 Cr, 10 Mn, 5 Ti	Campbell "A List of Alloys." A.S.T.M. Proceedings, Vol. 30, Part I, 1930	Tools
Bario, Soft	20	60 Co, 20 Cr	Campbell "A List of Alloys." A.S.T.M. Proceedings, Vol. 30, Part I, 1930	Tools
Bario, Sheet	1.2	90 Ni, 4.3 Cr, 0.3 Si, traces Co, Cu, Fe	Campbell "A List of Alloys." A.S.T.M. Proceedings, Vol. 30, Part I, 1930 "International Critical Tables," Vol. II, 1927	Tools
Bemit	0.27	96.91 Al, 2.0 Cu, 0.45 Mn	Ger.	Light alloy welded drawn or stamped parts
Bierman Tungsten Bronze	1.6	95 Cu, 3.4 Sn	"International Critical Tables," Vol. II, 1927	Strong corrosion resistant parts
Brass, Tungsten	4	60 Cu, 22 Zn, 14 Ni	"International Critical Tables," Vol. II, 1927	High strength brass parts
Brass, Tungsten	2	60 Cu, 34 Zn, 2.8 Al, 0.75 Ni, 0.7 Mn, 0.2 Sn	"International Critical Tables," Vol. II, 1927	High strength brass parts
Brix	1–4	75–60 Ni, 15–20 Cr, 5 Cu, 4 Si, 3 Ti, 2 Al, 2 B	"International Critical Tables," Vol. II, 1927	Heating elements heat and corrosion resisting parts
Bronze Tungsten	10	90 Cu	American Brass Co.	
Cletaloy Copper-Tungsten			Cleveland Tungsten, Inc.	Spot welding electrode
Complex English Metal	1.5	87 Sn, 6 Sb, 2 Ni, 2 Cu, 1 Zn, 0.5 Bi	"International Critical Tables," Vol. II, 1927	Bearings
Cooperite	14	80 Ni, 6 Zr	Brady "Materials Handbook," 1931 "International Critical Tables," Vol. II, 1927	Cutting tools
Deloro No. 4	15–20	45–50 Co, 25–30 Cr, 2.5–2.75 C	Campbell "A List of Alloys," A.S.T.M. Proceedings, Vol. 30, Part I, 1930	Tools
Duraloy "X"		Cr-Hi-W	Duraloy Co.	Chains in furnaces
Elkonite Grade 1W		Cu, W	P. R. Mallory Co., Inc.	Electrodes for welding steel
Elkonite Grade OW	50	50 Cu	P. R. Mallory Co., Inc.	Resisting welding electrode
Elkonite G-13		Ag-WC	P. R. Mallory Co., Inc.	Contactors
Elkonite Grade 1W3		Cu-W	P. R. Mallory Co., Inc.	Electrodes for spot welding steel
Elkonite Grade 100-W		Cu, W	P. R. Mallory Co., Inc.	Electrodes for spot welding copper and silver
Elkonite Grade		Ag, W	P. R. Mallory Co., Inc.	Electrodes for spot welding stainless steel
Elkonite Grade 5-W-3		Cu, W	P. R. Mallory Co., Inc.	Electrodes for welding steel

Name	W	Composition Others	Manufacturer or Reference	Uses
Elkonite (10-W-3)	77	24 Cu	P. R. Mallory Co., Inc.	Resistance welding electrode dies, valve seats, switches, bearing metals
Elkonite (10-W-3)	74.25	bal. Cu	General Electric Co.	Resistance welding electrode dies, valve seats, switches, bearing metals
Elkonite Grade 20-W-S		Cu, W	P. R. Mallory Co., Inc.	Welding electrodes
Elkonite Grade 30W3	80	20 Cu	P. R. Mallory Co., Inc.	Dies, welding dies
Fuchs Acid-Resisting Gold Alloy	10-15	75 Au, 10-15 Ni	Campbell "A List of Alloys," A.S.T.M. Proceedings, Vol. 30, Part I, 1930	Chemical equipment
Haynes Metal Soft	28	62 Co, 10 Cr	"International Critical Tables," Vol. II, 1927	Weld metal, tools
Haynes Metal Hard	40	45 Co, 15 Cr	"International Critical Tables," Vol. II, 1927	Weld metal, tools
Haynes-Stellite No. 1	11-14	29-34 Cr, Co 43 min.	Haynes-Stellite Co.	High speed tools
Haynes-Stellite No. 2		Co-Cr-W-C	Haynes-Stellite Co.	Tools for metal cutting
Haynes-Stellite No. 3	12-16	48-53 Co, 28-32 Cr, 2.5 C	Haynes-Stellite Co.	Tools, cutting tools, lathe tools, wear resisting castings
Haynes-Stellite No 4		C-Cr-Co-W	Haynes-Stellite Co.	Tools, special castings for wear and corrosion resistance
Haynes-Stellite No. 6	3-6	25-33 Cr, Co 55 min.	Haynes-Stellite Co.	High speed tools
Haynes-Stellite No. 12	7-10	25-34 Cr, Co 47 min.	Haynes-Stellite Co.	High speed tools
High-Speed Tool	5-12	6-12 Ti, 3-6 Si, 3-5 Al, up to 1.0 B, bal. Ni	Campbell "A List of Alloys," A.S.T.M. Proceedings, Vol. 30, Part I, 1930	Cutting tools, dies
High-Speed Wissler	15-40	15-50 Ni, or Co, 15-35 Cr, 0.5-2.5 B, 0.75-2.5 C	Campbell "A List of Alloys," A.S.T.M. Proceedings, Vol. 30, Part I, 1930	Cutting tools, dies
J. Metal (Stellite J-Metal)		Cr, Co, W	Haynes-Stellite Co.	Tool bits, milling cutter blades, boring and reaming blades
LN-14 Silver-tungsten			Cleveland Tungsten, Inc.	Spot welding electrode
Mallory HA Metal		W-Alloy	P. R. Mallory Co., Inc.	Electrical contacts
Mallory HB Metal		W-Alloy	P. R. Mallory Co., Inc.	Electrical contacts
Minargent	28.0	57-46 Cu, 40-32 Ni, 0.2-0.5 Al	Brady "Materials Handbook," 1931 "International Critical Tables," Vol. II, 1927	Silver solder, substitute for silver in silverware
Nickel-Tungsten	75-50	25-50 Ni	"International Critical Tables," Vol. II, 1927	Chemical apparatus, resistant to acids
Parr	3.3	66.6 Ni, 18 Cr, 8.6 Cu, 2 Al, 1 Mn, 0.2 Ti, 0.2 B	Campbell "A List of Alloys," A.S.T.M. Proceedings, Vol. 30, Part I, 1930	Chemical machinery parts
Partinum	0.8	96 Al, 2.4 Sb, 0.6 Cu, 0.2 Sn	"International Critical Tables," Vol. II, 1927	Light aircraft and automobile parts
Perceit	0-10	55-80 Co, 20-35 Cr	"International Critical Tables," Vol. II, 1927	High speed tools and dies

Name	W	Composition Others	Manufacturer or Reference	Uses
Platinoid A		60 Cu, 24 Zn, 14 Ni	United States Bureau of Standards Circ. 101, "Physical Properties of Materials 1924 Bamford and Harris, "Metallurgists' Manual," 1927	High resistance alloys, heating elements, thermocouples
Romanium	0.17	0.25 Cu, 1.75 Ni, 0.15 Sn. 97.43 Al	Judge "Engineering Materials," 1930	Light alloy parts
Sundeel	10	80 Au, 7 Ni	Campbell, "A List of Alloys," A.S.T.M. Proceedings, Vol. 30, Part I, 1930	Dental alloy
Ta W (Tantalum-tungsten)		Ta Plus W	Fansteel Metallurgical Corp., Inc.	Electronic tube parts, rectifier electrodes, chemical applications
Tantung		Alloy of Co, Cr and W, containing Ta carbide and Cb carbide	Fansteel Metallurgical Corp. Inc.	
W-Alloy	1	82 Al, 12 Cu, 4.5 Zn	"International Critical Tables," Vol. II, 1927	Light alloy castings
Wolframinium	0.05	98 Al, 1.4 Sb, 0.36 Cu, 1.0 Sn	Judge "Engineering Materials," 1930	Motor-car body work
K. Honda & T. Kase	42	32 Cr, 21 Mo, 4.2 N, 1.2-6 C	U. S. Patent 1,881,315 (1932)	Cutting tools
A. Kropf	10-60	1-40 Cr, 1-40 Ta, 5-30 Mo, 0.5-4 C	U. S. Patent 1,893,144 (1933)	Cutting tools

The following is a supplementary list of some of the commercial nonferrous tungsten alloys, other than those already described[12]:

Name	Tungsten	Composition	Reference	Uses
Brae-Cast	20	2.0 C, 1.5 Mo, 35 Cr, Cast 45 Co	Braeburn Alloy Steel Co.	Cutters, tools. Cast
Calliflex		W alloy	Callite Tungsten Corp.	Thermostats
Callinite		W alloy	Callite Tungsten Corp.	Facing alloy. High conductivity
Calmolloy		W alloy	Callite Tungsten Corp.	Grid wire
Cletaloy L-N-14		Ag-W	Cleveland Tungsten Inc.	Spot welding electrode
Delloy No. 4		Co-Cr-W	Delloy Metals	Cutting tools
Delloy No. 6		Co-Cr-W	Delloy Metals	Cutting tools
Delloy No. 7		Co-Cr-W	Delloy Metals	Cutting tools
Delloy No. 9		Co-Cr-W	Delloy Metals	Cutting tools
Diamond Alloy		Co-Cr-W-Mo	Brown Alloy Works	Cutters, tools
Elkonite 5W-53		Ag, bal, W	P. R. Mallory Co. Inc.	Resistance welding dies. Heat treatable
Elkonite 50S		Ag, bal, W	P. R. Mallory Co. Inc.	Electrical contacts
Elkonite 35S		Ag, bal, W	P. R. Mallory Co. Inc.	Electrical contacts
Excelite		Co-Cr-W	Excelite Co.	Cutting tools. Cast
Fastell NL		Cu, W	Fansteel Metallurgical Corp. Inc.	Electrical contacts. Sintered
Fastell UM		Ag, W	Fansteel Metallurgical Corp. Inc.	Electrical contacts. Sintered
Fastell UP		Ag, W	Fansteel Metallurgical Corp. Inc.	Electrical contacts, circuit breakers. Sintered
G. E. C. Heavy Alloy	90	7.5 Ni, 2.5 Cu	British General Electric Co. Ltd.	Screens in x-ray tubes. Sintered

Name	Tungsten	Composition	Reference	Uses
Gibsaloy Grade W	10–70	30-90 Ag	Gibson Electric Co.	Electrical contacts
Gibsaloy Grade NW	1–30	1–35 Ni, bal. Ag	Gibson Electric Co.	Electrical contacts. For high current densities
Heavy Alloy	76–90	1-16 Ni, 3-20 Cu	General Electric Co. Ltd.	For balancing crank-shafts of aero motors. Powder metals
Lamite Grade 1		Co-Cr-Mo-W	Vanadium-Alloys Steel Co.	Hard facing electrode. Cast
Lamite Grade 3		Co-Cr-Mo-W	Vanadium-Alloys Steel Co.	Hard facing electrode. Cast, corrosion resistant
Lamite Grade 6		Co-Cr-Mo-W	Vanadium-Alloys Steel Co.	Hard facing electrode. Cast, corrosion resistant
Lunorium	4	14.9 Cr, 0.9 Co, 55.6 Ni, 18.5 Mo, 5 Fe, 0.2 Mn, 0.4 Si 0.2 C		
Mallory 1000		Cu-W	P. R. Mallory Co. Inc.	Sintered Sp. Gr. 17
Niranium	2	28.8 Cr, 64.2 Co, 4.3 Ni, 0.1 Si, 0.2 C, 0.7 Al		
Red Arrow		Co-Cr-W	Latrobe Electric Steel Co.	Cutting tools. Cast.
Rexalloy	17	33 Cr, 44 Co,	Crucible Steel Co. of America	Cutting tools, gauges, wear strip. Cemented cast.
Stellit TTS No. 1		Co-W-Cr		Cutting tools. Hard sintered alloy.
Stellit TTS No. 2		Co-W-Cr		Cutting tools. Hard sintered alloy
Stoody 6		Co-Cr-W	Stoody Co.	Hard facing alloy. Impact resistant
Trimet		W	Callite Tungsten Corp.	Wire for sealing into glass
Wear Devil C-1		Co-Cr-Mo-W	Campion Rivet Co.	Hard facing welding electrode. Wear resisting
Wear Devil C-2		Co-Cr-Mo-W	Campion Rivet Co.	Hard facing welding electrode. Wear resisting
Wear Devil C-3		Co-Cr-Mo-W	Campion Rivet Co.	Hard facing welding electrode. Shock and impact resisting
Wilrich 600		Cr, W	Wilcox Rich Div. Eaton Mfg. Co.	Hard facing electrode. Corrosion resisting
Wilrich 625		Cr, W, Co	Wilcox Rich Div. Eaton Mfg. Co.	Hard facing electrode. Heat, abrasion and corrosion resisting

IV. Tungsten Carbides

Westgren shows that the amount of carbon taken up by the alloying elements to form carbides depends upon the relative atomic size or atomic radius of the elements concerned, as shown in the following table:

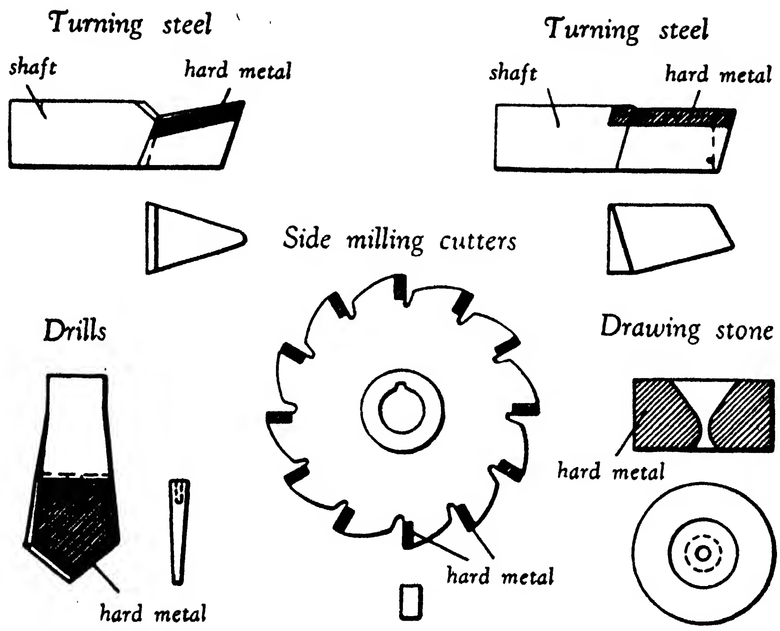
Carbide Phases of the Alloying Elements

	Titanium	Vanadium	Tungsten	Molybdenum	Chromium	Iron	Cobalt
Atomic Radius	1.45 Å	1.33 Å	1.36 Å	1.36 Å	1.27 Å	1.26 Å	1.25 Å
Carbide Phases	TiC	VC V_2C	WC W_2C	MoC Mo_2C	Cr_3C_2 Cr_7C_3 Cr_4C	Fe_3C	Co_3C

Titanium carbide is the most stable of the above-mentioned carbides. Vanadium carbide is more stable than the carbides of tungsten and molybdenum, which in turn are more stable than chromium carbide, iron carbide or cobalt carbide.

Some of the more common applications of tungsten carbide are as follows:

1. As dies for: tube drawing, extruding, bolt sizing, rivet heading, eyelet, swaging, wire drawing, burnishing; (lamp bases, metal radio tubes, shell cases, projectile jackets, cylinder liners, coated welding rod).

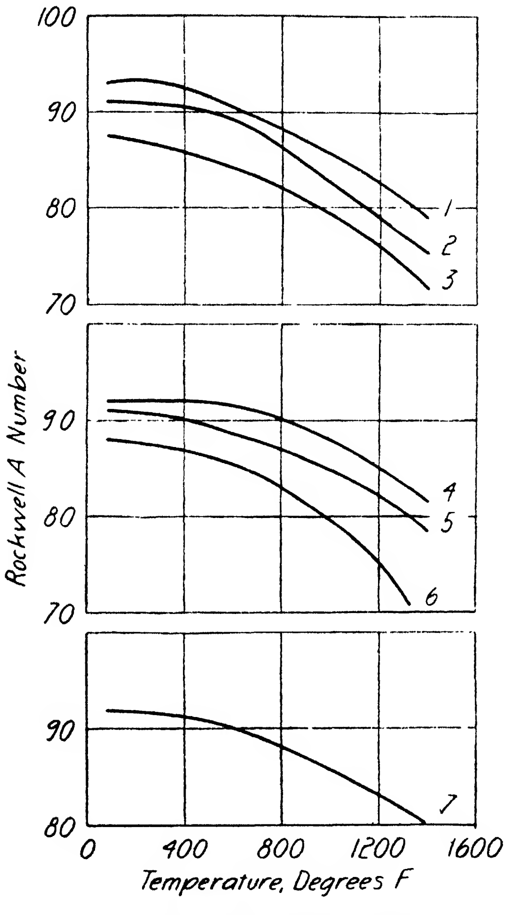


Tungsten carbide tools. *After F. Skaupy*

2. As tools for: turning, forming, cut-off, facing, milling cutters, reamers, end mills, boring, counterboring, punches, broaches, drills, slitting, saws, masonry and rock drills, glass cutting and drilling, spinning, burnishing, broaching, key-slotting.

3. As wear-resistant parts for: wire-forming and straightening, coil and spring machine parts, lathe centers and rests, valve seats, sandblast nozzles, thread guides, arbors, mandrels, micrometer jaws, snap and plug gauges, scale pivots, textile guides, bushings, fishing-rod guide rings, paper guides. The figure above shows some of the forms of the hard metal bodies (tungsten carbides) as used for different performances.

Carbide-to-carbide bearings have recently been developed by the Carboloy Co.[20]



Hardness of commercial cemented carbide alloys at high temperatures. *Curves: 1.* Predominantly WC with TiC plus 7% Co. *2.* Predominantly WC with TaC plus TiC 11% Co. *3.* Predominantly WC with TaC plus 13% Co. *4.* WC 94%, Co 6% (fine grain). *5.* WC 94%, Co 6% (coarse grain). *6.* WC 87%, Co 13% *7.* Predominantly WC with TaC plus TiC plus 6% Co. *After Engle.*

The shapes, forms and styles of tungsten carbides used for the above purposes are varied and multitudinous, and can be ascertained from the catalogues of various carbide manufacturers. However, they can be broken down to some fundamental types as illustrated below:

The carbides are generally brazed to steel shanks by the non-oxydizing flame of a torch. Cleanliness is absolutely essential for a good braze. The carbide-brazed tool must be cooled slowly by burying it in powdered charcoal, graphite or lime. For grinding, aluminous oxide wheels are for the steel shank and silicon carbide and diamond wheels for the carbide top.

Cemented tungsten-carbide tools retain their hardness at a bright-red heat, a temperature considerably higher than the softening temperature of high-speed steel. Obviously the cutting speed of cemented tungsten carbide is higher than that of high-speed steel. Its extreme hardness, coupled with resistance to abrasion, makes tungsten carbide the best cutting tool material now known. It is able to hold its edge at high speeds and at fine feeds, and to give smoother finish to the product than that obtained with high-speed steel.

The figure on p. 345 shows the hardness of commercial cemented carbide alloys at high temperatures.

Materials machinable with cemented tungsten carbide are indicated in the following table:

Non-metallic Materials
- Asbestos Compositions
- Bakelite
- Carbon
- Casein
- Celoron
- Celluloid
- Ebony Board
- Fabroid-fiber
- Hard rubber
- Ivory
- Magnesia compositions
- Micalex
- Micarta
- Textolite
- Wood

Non-metallic Abrasives
- Brick
- Cement
- Glass
- Marble
- Porcelain
- Slate
- Stone
- Similar materials

Non-ferrous Metals
- Aluminum
- Bearing Metals
- Brass
- Bronze
- Copper
- Die castings
- Genelite
- Low Ex
- Magnesium

Ferrous Metals
- Cast iron
- Invar
- Malleable iron
- Steel (only with cemented tungsten containing titanium carbide, tantalum carbide, or both added in small percentages)

A recent report of the American Society of Mechanical Engineers indicates average production increase through the use of tools of cemented carbides, in comparison with high-speed tool steels as follows: Cast iron, 10 to 200 per cent, the average being 60 per cent; steel, 10 to 80 per cent, the average being 35 per cent; aluminum, brass, bronze, other alloys, and other non-ferrous materials, from 15 to 500 per cent. Savings in cost of production, according to the same report, are as follows: Cast iron, from 5 to 75 per cent, averaging about 28 per cent; steel, from 5 to 50 per cent, averaging about 22 per cent; other materials, from 20 to 75 per cent, averaging from 20 to 40 per cent.

It has been mentioned that during the past six years the proportionate use of carbide tools for steel cutting has increased from 30 to 85 per cent.

According to Fred W. Lucht over 50 per cent of all metal removed by machinery is now being cut with carbide tools. Carbides are now either brazed to or clamped on steel shanks. Tools with "clamped-on" carbide tips are less subject to breakage, due to the absence of brazing strains; and since the brazing material melts at high temperature, mechanical mounting of the carbide tip does surmount this drawback. The three methods of brazing are: gas furnace brazing, oxy-acetylene torch brazing and induction brazing. Pure copper foil or bronze or silver alloy and borax flux are the materials used.

When used as tools and wear-resistant parts, the cemented carbide tip or insert is brazed to the steel tool with copper, silver solder or other commercial alloy. For dies, a relatively small amount of carbide is encased in that part of the steel die where wear-resistance is localized.

Setting of diamonds in core bits for drilling may be done by using tungsten carbide containing a considerable amount of cobalt as binder. Diamond dust of 20 to 300 mesh may be incorporated with a matrix of tungsten carbide containing 13 per cent cobalt (B.P. 359,637).

It has been reported that the Germans used cemented tungsten carbide for bullet cores in ammunition for anti-tank weapons in the African desert warfare.

In fact the 76-mm high velocity rifle carried by the Allied tank destroyers shoots a projectile whose core is of sintered carbide approximately 1½ in. in diameter and 5 in. long, making about 4 lb.

Tungsten carbide used for electrical contacts will be treated under the next heading.

The following is a list of trade names of some of the tungsten carbides manufactured in the United States:

Anchor-Tite
Arboga
Ardoloy
Armide
Blackor
Borium
Borod
Camite
Carboloy
Carmet
Dimondite
Dynite
Elmarid
Firthaloy
Firthite
Hartmetalle
Haystellite
Kennametal
Lohmanit
Midvaloy
Miramint
Perdurum
Phoran
Pobedit
Relit
Rexite
Strauss Metal
Talide
Teco
Thoran
Titanit (Cutanit)
Tizit
Vascoloy Ramet
Volumit
Walramite
Widia
Wig Metal
Wilcoloy
Willeys

The well-known among these are: Widia, the original cemented carbide developed by the Osram Lamp Works, Berlin; Carboloy, manufactured by the General Electric Co.; and Kennametal, manufactured by the McKenna Metals Co. The question whether Kennametal is superior to Carboloy still remains open.

V. ELECTRICAL EQUIPMENT

1. **Electric lamp filament.** The electric lamp industry, important as it is, requires less than 100 tons of tungsten a year. Tungsten filaments containing up to 2 per cent ThO_2 are used as cathodes for electronic tubes. The metallurgy of tungsten filament has been treated in Chapter IV.

2. **Contact Points.** Tungsten, as a metal in its pure form, is used very largely for contacts for the make-and-break electrical circuit. The metal used must be of a firm, close and equi-sized grain structure and must be 99.95 per cent pure. The process of sawing contact discs from tungsten rods by small abrasive wheels under jets of cold water was at one time developed by the Fansteel Products Co. In certain cases contacts are made from tungsten sheet, which in turn is manufactured by rolling small bars heated to a high temperature. Round discs or other shapes are punched from the hot-rolled sheets. The discs are then brazed to the proper backing of steel or copper to form the finished contacts. For the prevention of oxidation during welding, the surfaces may be coated with oil. Nickel foil or copper foil may be placed between the contact and its support before welding. There are now manufactured more than 200 different types of tungsten contact points. Among the important industrial devices using contacts are the following:

Airplane: Magnetos
Automative: Distributors, vibrator horns, magnetos, jump-spark contacts for gas engines
Bookkeeping Machines: Business machines of various types
Call Systems: Telephone
Controller: Controller devices for intermittent operation, street-signal lighting
Medical: Thermo-therapy apparatus, violet-rat machines, x-ray machines
Remote Control: Electrical devices for starting and stopping machines
Telegraphic: Ticker-tape machines, plant control typing machines
Time Systems: Bell for fire alarm, light signals, electric clocks
Thermostats: Incubators, temperature control, thermo-recording instruments
Type-setting: Automatic type-setting machinery
Vending Machines: Automatic vending machines, cash registers
Welding: Spot-welding machines

Tungsten carbide may also be used as electrical contacting materials (U. S. Patent 1,984,203). For contacts in heavier service an alloy of tungsten with a small percentage of silver is used. Carboloy (tungsten carbide bonded with cobalt) or wilcoloy (tungsten carbide bonded with osmium) is used for standard relay contacts for telegraph transmission.

Tungsten-copper compacts are used as contact materials. Compacts with a low copper content are chiefly used where the contacts just withstand the pitting and burning occasioned by the interruption of high currents. Compacts containing as much copper as tungsten are used for oil-immersed contacts and for sliding contacts.

VI. CHEMICAL COMPOUNDS

VI. 1. **Tungsten Bronzes**

These have been treated in Chapter V.

VI. 2. **Colors**[13]

It is of historical interest to note that the use of tungsten as coloring material for porcelain was practiced in the reign of Emperor Kang-hsi (A.D. 1662–1722). The Imperial Court of Emperor Kang-hsi ordered the best of the well-known porcelain kilns in the Province of Kiangsi at Ching Te Cheng (China) to manufacture eight forms of porcelain in the color of peach bloom. This peach-bloom color is particularly hard to produce on porcelain. It is neither pink nor red. It is a combination of pink and red with a suggestion of green. The Chinese call it Mei-Jen Chi, or maiden blush. As Chinese poets often compared "Maiden Blush" with peach bloom, the translation in English is peach bloom.

It is reported that 8,000 experiments on all kinds of minerals and metals were conducted before the tungsten color was discovered. The eight forms are as follows:

1. Chrysanthemum bottle
2. Amphora
3. Ring-necked bottle
4. Bottle with green dragon on the shoulder
5. Writer's water-stand
6. Flat-round painter's water coupe
7. Covered seal box
8. Apple-formed water jar

The first seven forms are on exhibition in the Metropolitan Museum of Art. In what form the tungsten was used is a mystery, but it has been proved by a German scientist, Dr. Paul Grünfeld, to be tungsten color. As the special kiln was fired entirely for use of the Imperial family and as it was not permitted to be made elsewhere, the "peach bloom" today is the most rare and most expensive porcelain on earth.

In this connection it is interesting to note that tungsten trioxide may be used as a yellow coloring matter in the ceramic industry, since permanent yellow glazes can be produced by fusion at 800° with lead silicate, with bismuth oxide, or with a mixture of zinc borate and silicate.[19]

It is well known in the color industry that basic dyes and certain of the acid dyes may be precipitated from solution by the addition of complex acids of the heavy metals, such as phospho-molybdic, phospho-tungstic, silico-tungstic, seleno-molybdic, etc., but the two commonly used by the color trade are phospho-molybdic and phospho-tungstic acids.

Before the discovery by the Badische Co. in 1913 that phospho-tungstic acid would precipitate basic dyes from solution, the pigments precipitated by organic compounds, such as tannic acid, or by inorganic compounds, such as aluminum phosphate or arsenate, had very little resistance to light. It is due to the researches of Arthur Linz[14, 15, 16, 17] of the Climax Molybdenum Co. that an adequate knowledge of the relative merits of both the molybdenum lakes and tungsten lakes is now available. It is significant to mention here that the work of Arthur Linz is based in no small measure on the fundamental research of Dr. Hsein Wu, a Chinese chemist, on the chemistry of phospho-molybdic and phospho-tungstic acids.[18]

The publications of the Climax Molybdenum Co. are freely used for the following discussion of the preparation and relative merits of the phospho-tungstic and phospho-molybdic acids.

"*Standard Procedure and Formulae: Sodium Tungstate Solution:* 10 per cent solution of $Na_2WO_4 \cdot 2H_2O$ prepared by dissolving a little more than 800 g of commercial $Na_2WO_4 \cdot 2H_2O$ in 8 liters of water, analyzing this for $Na_2WO_4 \cdot 2H_2O$ and diluting quantitatively to give a solution containing 10 g $Na_2WO_4 \cdot 2H_2O$ per 100 cc.

"*Phospho-Tungstic Acid Complex:* 1000 cc of the above solution (100 g $Na_2WO_4 \cdot 2H_2O$); 1.7 cc H_3PO_4 (85 per cent) sp. g. 1.71. Enough H_2SO_4 to give pH 3.0 when diluted to 10 liters, giving a 1 per cent complex on the basis of the $Na_2WO_4 \cdot 2H_2O$ contained.

"*Sodium Molybdate Solution:* 10 per cent solution of $Na_2MoO_4 \cdot 2H_2O$ prepared by leaching 725 g of Technical Molybdenum Trioxide (83 per cent MoO_3) with a solution of 34.3 g of NaOH, filtering and making up to eight liters, analyzing and diluting to give a solution containing 10 g $Na_2MoO_4 \cdot 2H_2O$ per 100 cc.

"*Phospho-Molybdic Acid Solution:* 1000 cc of the above $Na_2MoO_4 \cdot 2H_2O$ solution (containing 100 g of the salt), 2.37 cc H_3PO_4 (85 per cent) sp. g. 1.71. Enough H_2SO_4 to give pH 3.0 when diluted to 10 liters, making a 1 per cent complex on the basis of $Na_2MoO_4 \cdot 2H_2O$ contained.

"*Dye Solution:* 1 per cent solution of the dye in question prepared by dissolving 10 g of the dyestuff in a liter of water and enough glacial acetic acid to give pH 3.0. Heat for an hour at 60–70° to insure solution before precipitating.

"*Precipitation:* Lake is precipitated at 60–70° while stirring by adding the complex as rapidly as necessary to keep the temperature within the range. Usually requires 15 minutes. Clear up excess dye as described, heat to boiling and boil for 20 minutes. Clear up excess dye again, allow to settle and filter without washing. Dry in oven at 40–50°.

"1. Molybdenum lakes require more careful control in preparation but, on being thus controlled, are as easy to handle as tungsten lakes.

"2. Molybdenum lakes have a lower specific gravity, higher oil absorption, greater strength, and are easier to grind than tungsten lakes.

"3. Tungsten lakes are slightly brighter in top tone.

"The tungsten lakes, as well as the lakes containing maximum tungsten and minimum molybdenum, fade on exposure. The molybdenum lakes, as well as those containing maximum molybdenum and minimum tungsten, darken on exposure. From this there can be concluded only the fact that it is not a question of relative fastness, but a question as to whether the consumer prefers a change in color in the direction of fading or in the direction of darkening."

It has been mentioned elsewhere that the basic difference between tungsten and molybdenum pigments is that the former possess greater brilliancy and better permancy than colors made from the same dyes with molybdenum, but this better brilliancy and permancy are obtained at the sacrifice of tinting strength and at a higher cost per pound. For this reason, most of the so-called tungsten colors that are on the market are combinations of tungsten and molybdenum, though for certain purposes tungsten or molybdenum alone is employed.

These pigments are marketed under such trade names as, "Consul", "Fanal" and "Brillfast". The lakes or pigments containing tungsten and molybdenum possess the valuable property of being quite insoluble in water and linseed oil so that they can be used in both oil and water paints.

Phospho-tungstic and phospho-molybdic pigments are used mostly in the printing-ink industry. The paint, enamel, rubber, wax and paper industries all use appreciable quantities of these pigments.

According to the United States Tariff Commission Report, the United States 1940 production of phospho-tungstic pigments was 814,611 pounds and that of phospho-molybdic toners and lakes was 50,556 pounds. The series of blue-colored oxides, intermediate between the di and trioxides, have been used as blue pigments under the commercial names wolfram-blue, mineral blue and blue carmine.

VI. 3. Miscellaneous Tungsten Compounds

As adsorbent gel, tungstic oxide has been used alone or in combination with silica gel. Tungstic acid may be used as a special mordant and coloring agent in the porcelain industry. Sodium tungstate, mixed with a small amount of ammonium phosphate and ammonium sulfate, is used for flameproofing and waterproofing materials. The tungstate of calcium and of other metals have been applied in preparing screens for x-ray work. It is reported that there has been developed a new glass based on the use of one of the tungsten salts, with a much higher refractive index. This new glass is specially used in aerial camera lenses. Sodium tungstate is used as a decorticator in preparing raw fibers for manufacturing. Lead, zinc, and barium tungstates may be used as substitutes for white lead. Sodium tungstate has been used for delustering rayons. Tungstates were employed in Germany to fireproof rayon and staple fiber for the electrical industry. The fiber was treated with solutions of sodium tungstate and tin chloride, leaving a deposit of insoluble tin tungstate on the material. Mixtures of tin and aluminum tungstate were also used, either alone or in combination with phosphates.

The complex derivatives of tungsten are good precipitators of albuminoids and are therefore invaluable as tanning agents. Moreover, skins mordanted with tungsten derivatives will take up basic colors in a uniform manner. Applications are also found in dyeing textiles, coloring glass and paper, weighting silks, and making fluorescent powders. Sodium paratungstate may be used as a soaking agent for dried and salted hides and skins.

Tungsten Carbonyl $W(CO)_6$ may be used for coating cast iron pipes or steel pipes, rendering them resistant to acid and high temperature. Its manufacture is described in U. S. Patents 1,894,239 and 1,921,536.

As a catalyst for the hydrogenation of carbonaceous materials and the cracking of oil, tungsten has been found useful. This is embodied in the following U. S. Patents: tungsten with or without molybdenum [1,948,058-(1934)], [1,894,926 (1923)]; tungsten disulfide with or without ferrous sulfide [1,965,956 (1934)], [2,127,383 (1938)], [2,227,672 (1941)], [2,280,258 (1942)]; tungsten iodide [2,028,348 (1936)]; tungstic acid mixed with chromic acid; manganese carbonate and zinc sulfide [1,922,499 (1933)]; platinum sulfide and tungsten sulfide [1,965,956 (1934)]; tungsten sulfide and iron [2,280,258 (1942)]; tungsten salts, such as hydroxides, carbonate, halides and phosphates [2,287,891 (1942)].

It is reported that tungstic acid constitutes one of the ingredients used in processing toluol to TNT. Magnesium tungstate is one of the ingredients called phosphors, used in the fluorescent lamp.

VII. Miscellaneous Applications

As a thermal electron emitter, tungsten is used in radio valves and electron microscopes, either as such or with its surface covered with thorium.

On account of its high elasticity, tungsten wire is particularly suitable for use in galvanometers and telescopes as crosshairs, and for surgical stitching. Tungsten is used for making helical springs for use in valves and other devices.

It appears in razor blades, watch springs, piano wires and sounding boards and cathodes of x-ray equipment. Tungsten metal rods are used in glass-blowing for making holes in glass after fusing. Due to its coefficient of expansion, tungsten is used for carrying the current through "Pyrex" and similar high-temperature glasses into transmitting tubes. It is also used as the heating element for vaporizing metals to make metallic mirrors. Tungsten rod, generally around 0.060 in. diameter, is used also for a class of welding known as the "atomic hydrogen process." Dumpelmann and Ehlers, U. S. Patent 2,280,223 (1942) recommended the use of a coating for welding rod, made up of a mixture of tungsten carbide, molybdenum carbide, vanadium and kaolin or quartz. Tungsten is used in safe and vault walls. The use of tungsten steel for high-temperature work such as gas turbines and generators is still new and is not widely known. Tungsten wire can be used for the winding of electric tube furnaces. For a number of electrochemical processes, tungsten electrodes have been used. Armor-piercing projectiles, erosion-resisting gun liners and bullet cores are alloyed with tungsten.

An alloy (U. S. Patent 1,703,577) of lead, antimony, tin, copper and tungsten or of lead, zinc, iron, aluminum, copper and tungsten is suitable for journal bearings or can be used for the manufacture of bullets or shots. Carbonitride of tungsten (U. S. Patent 1,803,276) can be used as cutting tools. A steel with approximately 0.65 per cent carbon and from 1 to 3 per cent tungsten has been used for erosion-resisting gun linings. It has been mentioned that the life of rails can be prolonged 5 years by the addition of 0.3 per cent tungsten to the steel used.

M. U. Schoop* proposed that coatings of tungsten or tungsten carbide can be applied by means of his "Schoop-Pistole", that is, tungsten or tungsten carbide in the form of powder or wire can be metallized and sprayed onto any surface by means of an electric arc and a metallizer with a mixture of nitrogen and hydrogen. To prevent oxidation of the tungsten used air must be excluded as much as possible.

An alloy, containing 95 per cent platinum and 5 per cent tungsten, was widely used in Germany during the war as a substitute for iridium platinum in the manufacture of ignition and magneto contacts.

VIII. PURE TUNGSTEN OF COMMERCE

The pure tungsten of commerce is generally supplied in any of the following five forms:

---

* Schoop, M. U., "Über die Herstellung von überzügen aus Wolfram bzw. Wolfram-Karbid mittels der "Schoop-Pistole", *Korr u. Metallsch,* **18,** No. 7 p. 243-4 (1942).

1. Powder, of various mesh sizes, for chemical and electrical purposes.
2. Rods for supports, springs and contacts.
3. Sheets.
4. Wires for lamps and radio tubes.
5. Special forms, such as discs, contacts and vessels.

References

1. Gill, J. P., "Tool Steels", American Society for Metals, Cleveland, Ohio (1944).
2. Grossmann, M. and Bain, E. C., "High Speed Steel" (John Wiley and Sons), New York, 1931.
3. Lantsberry, F. C. A , "High Speed Steel", *Trans. Am. Soc. Steel Treat.*, **11**, 711-729, 803 (1927).
4. Sisco, F. T., "The Manufacture of Electric Steel" (McGraw-Hill Book Co), New York, 1924.
5. Cregg, J. I., "The Alloys of Iron and Steel", pp. 138-151 (McGraw-Hill Book Co.), New York, 1934.
6. Lantsberry, F. C. A., Ibid.
7. Sisco, F. T., Ibid.
8. "Metals Handbook" (1949 Edition) p. 502 (American Society for Metals), Cleveland.
9. *American Machinist*, **96** (February 21, 1940).
10. Wissler, W. A., "Alloys of Cobalt, Chromium, and Tungsten", *Metal Progress*, 131-138 (Aug. 1939).
11. Wulff, John, "Powder Metallurgy" pp 474, 476 (American Society for Metals), Cleveland, 1942.
12. Woldman, N. E. & Dornblatt, A. J , "Engineering Alloys" (American Society for Metals), Cleveland, 1936
13. Mattiello, Joseph J., "Protective and Decorative Coatings", Vol. II, Chapt. 1, 2 and 7 (John Wiley and Sons), New York, 1942.
14. "Molybdenum in Lakes, Pigments and Drying Oils", Climax Molybdenum Co., LaboratoryReport, October, 1936.
15. "Investigation of the Preparation of Molybdenum Orange", Climax Molybdenum Co., Laboratory Report, June, 1938.
16. "Investigation of Basic Dyes by Phospho-Molybdic and Phospho-Tungstic Acids", Climax Molybdenum Co., Laboratory Report, February, 1938.
17. Linz, Arthur and Coffer, L. W., "Tungstate and Molybdate Toners", *The American Ink Maker* (Sept., Oct., Nov., 1939).
18. Wu, Hsein, "Contribution to the Chemistry of Phospho-molybdic Acids, Phospho-tungstic acids and Allied Substances", *J. Biolog. Chem.*, **43**, (1920).
19. Granger, *Compt. rend.*, **140**, 935 (1905).
20. Brams, S. H., "Tungsten Carbide Machine Parts", *Iron Age*, 55-57, (Sept. 27, 1945).

Chapter VIII

Substitution of Tungsten

The imminence of possible shortage of tungsten, especially under war conditions, coupled with the violent fluctuation of the price of tungsten, has given impetus to metallurgical search for at least a partial substitute for tungsten. Since 70 to 85 per cent of tungsten consumption is in high-speed steels, the question of substitution lies in finding and in determining the amount of a metal which can partially replace the tungsten component of the high-speed steel alloy.

Molybdenum has to a great extent the chemical and physical qualities of tungsten. Both belong to the chromium group, have high melting points, and can impart "red hardness" to the steel. The atomic weight of tungsten is 184 and that of molybdenum is 96; consideration of these atomic weights has led to the too-broad assumption that "molybdenum will replace tungsten in high-speed steel in the proportion of one to two", which, as will be seen later, has to be greatly modified. Development of partial substitution of molybdenum for tungsten in the high-speed steel of the "18-4-1" type (18 per cent tungsten, 4 per cent chromium and 1 per cent vanadium) within the last fifteen years has produced many steels of various compositions which, in some cases, have given good results, even excelling those of "18-4-1". In these new types of high-speed steel, the principal alloying element is molybdenum, tungsten being used in minor quantities for its powerful auxiliary effect. The molybdenum-tungsten high-speed steels are particularly attractive because of their lower cost of material and of heat treatment, their hardening temperatures being substantially lower than those used for "18-4-1".

Zay Jeffries[1] has treated the subject of substitution of molybdenum for tungsten comprehensively in his report as Chairman of the Advisory Committee on Metals and Minerals of the National Research Council, National Academy of Sciences, excerpts from which are given as follows:

"The composition of high-speed steel 'T-1', and three types of molybdenum high-speed steel, in the order of decreasing tungsten content, available for possible substitution, are listed below:

	T-1	M-1	M-2	M-3
Tungsten	18	5.0–6.0	1.5	—
Molybdenum	—	3.5–5.5	9.0	7.0–9.0
Chromium	4	3.5–4.5	4.0	4.0
Vanadium	1	1.25–1.75	1.0	2
Carbon	0.70	0.60–0.90	0.80	0.80

"M-1, M-2, M-3 have good cutting properties and, apart from differences and difficulties in processing, are suitable substitutes for 18-4-1. Complete substitution of 18-4-1 by the compositions given would save one-half to three-quarters of the tungsten consumed in 18-4-1.

"The table above gives merely types of substitution; the table below gives a fuller account, though it is suggestive and not restrictive:

	Present Types of Tungsten High-Speed Steels					Suggested Molybdenum Substitutions				
	% W	% Cr	% V	% Co		% W	% Mo	% Cr	% V	% Co
T-1	18	4	1		M-3	—	7–8	4	2	
T-2	18	4	2		M-4	—	9	4	3	(high C)
T-3	14	4	2		M-5	1.5	9	4	2	
					M-2	1.5	9	4	1	
					M-1	5–6	3.5–5 5	3.5–4.5	1.25–1.75	
					M-7	6	6	4	1.5	
TC-1	18	4	1	5	M-6	5.5	4.5	4.5	4	
TC-2	18	4	2	8	M-8	—	8	4	1	2.5B
TC-3	14	4	2	5	M-9	—	8	4	1.5	8B
					M-10	1.5	8	4	1	5
					M-11	1.5	6.5	4	2	5
					M-12	1.5	8	4	2	8
					M-13	6	6	4	1.5	6

"Some manufacturers and users do not regard the suggested molybdenum substitutes as proper, while others do; it has been questioned, for example, whether M-7 is a proper substitute for T-1 in all applications. Certain of the suggested substitutes are expensive; others are 'special purpose steels' not of wide usefulness; again, others are difficult to manufacture. The usefulness of boron additions has been questioned; it is said that cobalt increases the difficulties in decarburization.

"The substitution of the M-type steels noted will require changes in processing except, it is reported, in the case of M-1 which may be heat-treated in the same equipment and with the same technique as T-1. Heat treatment temperature schedules vary somewhat from those employed for tungsten steels, but these are known. Steels of the types M-2 and M-3 have a greater tendency to decarburize than the tungsten types T-1, T-2 and T-3 or the molybdenum-tungsten type M-1, and for this reason their surface must be protected during manufacture and during heat-treatment; for tools to be ground after heat-treatment this is not a serious difficulty. Suitable protection is afforded by a borax or copper-base paint coating or by a reducing atmosphere so adjusted as to avoid excessive carburization; special atmospheres require special furnaces which are now difficult to procure; salt baths have been useful in heat-treatment in this respect. This difficulty will be the greater for the very large number of small users of high-speed steel and the lesser for the small number of large users, for the latter often already possess the necessary equipment, whereas the former do not.

"**Alloy Tool Steels.** Listed below are a number of compositions of low-alloy tool steels containing tungsten, with suggested molybdenum substitutes; substitution should be approached with caution and adopted only after trial.

"It is very important to note that the substitutes suggested are molybdenum substitutes only. There are other and, it is said, better substitutes containing neither tungsten nor molybdenum. The recommendations made in this section, therefore, have far less weight than those in other sections. The amount of tungsten consumed in these steels is small.

Low-alloy Steels Containing Tungsten		Suggested Molybdenum Substitutes	
T-4	0.85–1.0 C, 0.30 Si, 1.3 Mn, 0.45 Cr, 0.45 W, 0.10–0.25 V	M-14	0.95 C, 0.30 Si, 1.3 Mn, 0.50 Cr, 0.25 Mo, 0.20 V
		(Note:	See comment above on non-molybdenum substitutes)
T-5	0.45 C, 0.3 Mn, 0.30 Si, about 2.0 W, 1.5 Cr, 0.25 V	M-15	0.5 C, 0.9 Mn, 1.9 Si, 1.3 Mo, 0.3 V, 0.2 Cr
		M-16	0.5 C, 0.7 Mn, 1.6 Si, 0.6 Mo, 0.2 V
		M-17	0.6 C, 1.0 Mn, 2.0 Si, 0.5 Mo, 0.3 V
		M-18	0.5 C, 1.0 Mn, 2.0 Si, 1.35 Mo, 0.5 V
		M-19	0.5 C, 0.4 Mn, 1.0 Si, 0.5 Mo
		M-20	0.45 C, 0.3 Mn, 0.3 Si, 1.0 Mo, 1.5 Cr, 0.25 V
		M-21	0.6 C, 0.8 Mn, 0.3 Mo, 1.9 Si
		(Note:	See comment above on non-molybdenum substitutes)
T-6	1.30 C, 3.6 W, 0.25 Cr	M-22	1.25 C, 2.0 Mo, 0.25 Cr
		M-23	1.1 C, 0.3 Si, 1.3 Mo, 1.2 Cr, 0.4 W, 0.3 V
		(Note:	See comment above on non-molybdenum substitutes)
T-7	1.25 C, 0.3 Mn, 0.75 Cr, 0.2 V, 1.4 W	M-24	1.3 C, 0.3 Mn, 0.75 Cr, 0.2 V, 0.75 Mo
		(Note:	See comment above on non-molybdenum substitutes)

"**Stellite.** About 2 per cent of the yearly consumption of tungsten is employed in the manufacture of stellite. Stellite is a non-ferrous alloy of which several compositions are made. One of these is: Co 45–50, Cr 31–35, W 12–15. Other compositions run toward higher cobalt (up to 68 per cent) and lower tungsten (down to 3 per cent), with chromium remaining practically constant. Such tool materials, owing to the small quantities used, consume but little tungsten; because of their unusual cutting qualities their use offers some opportunity to conserve tungsten. The substitution of molybdenum for tungsten has been attempted with but little success, and this, or other, substitute in stellite is not recommended.

"**Tungsten Carbide Tools.** About 5 per cent of the yearly consumption of tungsten is employed in the manufacture of tungsten carbide compositions. Other carbide tool materials containing tantalum carbide, titanium carbide, etc., together with tungsten carbide, are in wide use. These various types of carbide tool materials find varied, and often specialized, uses; occasionally they are not interchangeable. Such tool materials, owing to the small quantities used, consume but little tungsten; owing to their unusual cutting qualities, their use offers an opportunity to conserve tungsten, particularly in single cutting-point application where their use could be increased.

"**Die Steels For Hot Working.** There are listed below a few compositions of die steels containing tungsten, used mainly in the hot-working of metals. A few substitutes for them are suggested containing molybdenum with less or with no tungsten. There are many other die steels containing tungsten, not listed; important substitutes containing neither tungsten nor molybdenum are not listed. Substitutes should be approached with caution and adopted only after trial. The amount of tungsten consumed in these steels is minor.

Die Steels Containing Tungsten	Suggested Molybdenum Substitutes
T-8 0.3 C, 5.0 W, 5.0 Cr	M-25 0.3 C, 5.0 Cr, 0.9 Si, 1.25 Mo
T-9 0.3 C, 1.25 W, 5.0 Cr, 1.25 Cr	M-26 0.35 C, 3.5 Cr, 6.0 Mo, 0.75 V, 1.0 W
T-10 0.3 C, 3.25 Cr, 9.0 W, 0.25 V	M-27 0.6 C, 3.5 Cr, 8.5 Mo, 1.75 V
	(Note: See comment above on non-molybdenum substitutes)

"**Valve and Valve Insert Steel.** Many exhaust valve insert seats and the exhaust valves for aircraft engines are made from an alloy containing tungsten as follows: 0.45 C, 0.70 Mn max., 0.50 Si, 14.0 Ni, 14.0 Cr, 2.5 W, 0.35 Mo; both Wright and Pratt and Whitney are using this steel; any change at the moment would be very inadvisable. A composition is available for insert seats closely corresponding to this, except silicon ranges from 2.75 to 3.25.

"It is reported that relatively large quantities of the following molybdenum-steel are being sold for use as valve-insert and exhaust-valve steel and as intake-seat steel: 0.70 C, 0.50 Mn, 1.0 Si, 3.0 Cr, 5.0 Mo.

"Intake valves for aircraft engines are now made from alloys of the following compositions:

(1) 0.55 C, 0.30 Mn, 3–4 Cr, 13.5 W
(2) 0.30 C, 0.50 Mn, 12–13.5 Cr, 2–3 Si, 7–8.5 Ni

"It has been said that these two compositions are not to be taken as interchangeable for this application; the Pratt and Whitney engine requires (1) and the Wright (2); but other engineers believe that all intake valves may be made of (2) if the necessity arises.

"It is reported that a satisfactory substitute for intake valves in lower horse-power engines (but not for the present high horsepower engines) has been employed, of the following composition: 1.35 C, 12.25 Cr, 0.65

Mo, 3.0 Co. The use of this alloy is slight; the substitution of tungsten by cobalt may be questionable on the basis of availability of cobalt. Work is now actively under way on possible substitutes for (1) and (2) for the newer engines. It is suggested that (2) may replace (1), or *vice versa*, in accordance with the availability of tungsten, chromium and nickel.

"**Armor-Piercing Projectiles and Bullet Inserts.** The substitution of molybdenum for tungsten in these materials is now under study. Colonel S. B. Ritchie, of Watertown Arsenal, reports that complete substitution can be effected if the necessity arises, provided that some sacrifice in ballistic efficiencies can be tolerated and production difficulties, which may arise in the new materials, can be satisfactorily handled. If this should be done, it will go far to avoid a shortage of tungsten. There is no requirement of tungsten in armor plate, according to Colonel Ritchie.

"**Magnet Steels.** The total tungsten consumption for permanent magnets is very small. Formerly, large quantities of permanent magnet steel were used of the following composition: tungsten 5–6 per cent; carbon 0.70 per cent. This has been largely replaced and can still further be replaced by a chromium steel of the composition: chromium 3.5 per cent, carbon 0.95 per cent.

"The newer permanent magnet compositions of aluminum, nickel, cobalt and iron have replaced large quantities of the two compositions above. These are cast or sintered (powders) of the following compositions:

(1) 12 Al, 20 Ni, 5 Co, balance Fe
(2) 10 Al, 17 Ni, 12 Co, 6 Cu, balance Fe

"The chromium magnet steel listed above will probably best serve the purpose of conservation, except in special applications where the special properties of the aluminum-nickel-cobalt composition make them irreplaceable.

"**Electrical Application.** About 1.5 per cent of the tungsten consumed is employed in the manufacture of electric equipment—lamps, X-ray tubes, radio tubes, etc. The quantity is insignificant and substitution of molybdenum is not possible in most of these uses.

"**Tungsten Reclamation.** It is said that appreciable amounts of tungsten could be made available for use by more complete segregation and reclamation of tungsten scrap, and it is suggested that a campaign with this aim should be forwarded."

The principal brands of molybdenum-tungsten high-speed steels are as follows:

Brand Name	Company
"Momax"	Cleveland Twist Drill Company
"Mo-Tung"	Universal-Cyclops Steel Corp., Bridgeville, Pa.
"LMW"	Allegheny-Ludlum Steel Corp., Pittsburgh, Pa.
"Bethlehem HM"	Bethlehem Steel Company, Bethlehem, Pa.
"Mo-Cut"	Braeburn Alloy Steel Corp., Braeburn, Pa.
"Star Max"	Carpenter Steel Company, Reading, Pa.
"Molite MT"	Columbia Tool Steel Company, Chicago Heights, Ill.
"Rex T-Mo"	Crucible Steel Co. of America, New York, N. Y.
"Di-Mol"	Henry Disston & Sons, Inc., Philadelphia, Pa.
"Rex T-Mo"	Halcomb Steel Company, Syracuse, N. Y.
"Mogul"	Jessop Steel Company, Washngton, Pa.
"Tatmo"	Latrobe Electric Steel Company, Latrobe, Pa.
"S. T. M."	Simonds Saw & Steel Co., Lockport, N. Y.
"Vul-Mo"	Vulcan Crucible Steel Company, Aliquippa, Pa.

As the "Mo-Max Family of Molybdenum-Tungsten High Speed Steels" are better known in the market, a brief description of their various types is now given.[2]

Analyses of Comparative Types of High-Speed Steels

	Type 1	Type 2	Type 3	Type 4	Type 5	Typr 6	Type 7
Molybdenum—Tungsten High Speed Steels ("Mo-Max")							
Carbon	0.80 (a)	1.00	0.40	0.80	0.85	0.88	0.88
Molybdenum	8.75	8.75	5.75	8.75	6.50	9.50	8.25
Tungsten	1.50	1.50	1.00	1.50	1.50	1.50	1.50
Chromium	3.75	3.75	3.75	3.75	3.75	3.75	3.75
Vanadium	1.00	2.00	0.70	1.00	2.00	1.00	2.00
Cobalt				5.00	5.00	8.00	8.00
Comparable Types of High-Tungsten Steels							
Carbon	0.70 (a)	0.82	0.35	0.70	0.70	0.75	0.82
Tungsten	18.00	18.50	14.00	18.00	14.00	18.00	18.50
Molybdenum		0.70					0.70
Chromium	4.00	4.00	0.00	4.00	4.00	4.00	4.00
Vanadium	1.00	2.00	0.50	1.00	2.00	1.00	2.00
Cobalt				5.00	5.00	8.00	8.00

Type 1 is probably the most easily machinable of all high-speed steels. Increased vanadium together with the addition of cobalt tends to decrease the machinability of high-speed steels, especially in grinding. Type 2, being high in carbon and vanadium, is particularly useful where great hardness and resistance to abrasion are required, as in the case of reamers and broaches. Type 3 is a hot die steel, useful for hot-coining, pressing, and extruding. Types 4, 5, 6 and 7 are all cobalt high-speed steels suitable for the most severe duty.

Red-M-2. This type of tungsten-molybdenum high speed steel has been developed during the last ten years. Its composition is: W 6.40, Mo. 5.00, Cr 4.15, V 1.90, Co .83. It has good red hardness and outstanding toughness characteristics. While tests at the mill indicate a 20 per cent superiority over the 18-4-1 type in cutting efficiency, performance in the field has shown even greater improvement*. Typical applications are

---

* Private information from Mr. R. W. Warren, metallurgist, Crucible Steel Co. of America.

lathe, planer and boring tools, milling cutters, hobs, form and threading tools, twist drills, end mills, taps, reamers, broaches and chasers.

In Great Britain under war conditions, the molybdenum-tungsten high speed steel has been perforce adopted. Iron and Steel Order No. 19 gives, among others, two typical grades, as follows:

	"Substitute 66"	"Substitute 94"
Molybdenum	5.0 to 6.0 per cent	8.5 to 9.0 per cent
Tungsten	5.5 to 6.5 " "	3.5 to 4.5 " "
Chromium	4.0 to 5.0 " "	3.5 to 4.5 " "
Vanadium	1.25 to 1.50 " "	1.25 to 1.50 " "

"Within the last four years considerable effort has been made in both Russia and Germany* to find low tungsten compositions which would compare favorably with the standard 18-4-1 type. According to these reports it is apparent that a satisfactory high speed steel can be made containing as low as 8.00 per cent tungsten with additions of less than 1.00 per cent molybdenum, providing the vanadium and carbon contents are suitably increased. The toughness of these steels is not comparable to those with high tungsten contents and the difficulties encountered in heat treatment are somewhat greater."

Among the many European investigators who have worked on the partial substitution of tungsten in high speed steels may be mentioned Herbert Briefs[3], F. M. Capuano[4], F. Homma[5], A. Linley[6], and H. Kalpers[7]. Briefs has shown that the 18 per cent tungsten content of the standard type could be appreciably reduced by an increase of vanadium or molybdenum content without impairing the cutting capacity. For instance, a steel containing 4.0 per cent chromium, 2.3 per cent molybdenum, 2.75 per cent vanadium, 2.3 per cent tungsten and 0.9 per cent carbon is particularly well suited for milling drilling tools. According to Capuano, a steel containing up to 12 per cent tungsten, up to 4.5 per cent vanadium, 1.0 per cent molybdenum and up to 4.5 per cent chromium, and a steel containing up to 11.5 per cent tungsten, up to 2.7 per cent vanadium, 0.6 per cent molybdenum and up to 4.5 per cent chromium are better than—or at least equal to a steel containing 18 per cent tungsten. Kalpers has investigated the following types of high-speed steel:

	I	II	III	IV
Carbon	0.77	0.76	0.79	0.75
Tungsten	10.93	19.02	11.70	18.40
Vanadium	0.99	0.79	1.35	0.98
Molybdenum	0.70	0.20	0.68	0.55

---

* Fizia, R., Gebhard, K., Rapata, F., and Scherer, R., *St. and E.*, Vol. **95** (1939), 985, "Effect of Vanadium and Chromium Upon Low Alloy High Speed Steel".

Osipov, *Novosti Tekhniki* (1939), No. 23, No. 24, p. 28–9, "New High Speed Tool Steel".

Minkevich, N. A. and Ivanov, O. S., *Metallurg*, No. 1 (1940), **31** "New Low-Alloy High Speed Steels".

The conclusions of his investigation are: an increase in the molybdenum content from 0.13 to 1.99 per cent rendered the cutting performance four times higher; an increase in the vanadium content from 0.79 to 1.2 per cent permitted a reduction in the tungsten content from 19 to 10.25 per cent; tungsten-rich steels of low alloy type are comparatively inferior.

The composition of one of the so-called "emergency high-speed steels" developed in Germany is as follows: 1.35 C, 4.3 V, 4.25 Cr, 11.5 W and 0.09 per cent Mo.

Other Substitutes. Zirconium may be used to alloy with steel for making armor plate, armor-piercing projectiles and bullet-proof metal. Cooperite, a patented alloy of zirconium with nickel, is extremely hard and is well adapted to making cutting tools. Both tungsten carbide and stellite may be considered as partial substitutes, since in these forms a smaller amount of tungsten is capable of doing the same work as a larger amount in high-speed tool steels.

Carbide and High Speed Steel Tip Tools and the Use of Carbide[8]. Under the pressure of material shortages, tipped tools may be substituted for solid shank tools. For brazing the carbide or high speed steel tips onto the steel shank, powdered silver-copper or copper alloys, mixed with the required flux may be used. Also, in the machining of non-ferrous metals, cast iron or steel, substitution of cemented carbide for high speed steel has been finding favorable reception.

According to E. Houdremont and H. Schrader the following are good substitutes for high speed steel.

U. S. Patent 2,209,622 (1940): 1.10–1.6 per cent C, 1.0–6.0 per cent Cr, 1–5 per cent Mo, 2.6–6.0 per cent V, 1–4 per cent W.

U. S. Patent 2,209,623 (1940): 0.6–1.0 per cent C, 3.0–6.0 per cent Cr, 2.0–4.0 per cent Mo, 2.0–3.0 per cent V, 1.0–4.0 per cent W.

U. S. Patent 2,230,687 (1941): 1.2–1.5 per cent C, 3–5 per cent Cr, at least 3 and less than 5 per cent Mo, 4–6 per cent V, 0.2–5.0 per cent Co.

U. S. Patent 2,278,315 (1942): 1.0–1.6 per cent C, 1.0–6.0 Cr, more than 1.0 per cent and less than 5.0 per cent Mo, 2.0–6.0 per cent V, more than than 1.0 per cent and less than 5.0 per cent Mo, 2.0–6.0 per cent V, and W amounting to at least 50 per cent of Mo and ranging 1.0–4.0 per cent.

References

1. "Substitution of Molybdenum for Tungsten", *Mechanical Engineering*, 798-800 (Nov. 1941).
2. Emmons, J. V., "The Tungsten Situation", *Metal Progress*, 427–431 (April, 1941).
3. Briefs, Herbert, "High Speed and Alloy Tool Steels from the Point of View of Economy in Strategic Materials", *Werkstattstech. u. Werksleiter*, 36, 297–9 (1942); *Chem. Zentr.*, I, 2133 (1943).
4. Capuano, F. M., "High-Speed Steels", *met. ital.*, 34, 1–4 (1942); *Chem. Zentr.*, II, 1843 (1942).
5. Homma, F., "High-Speed Tools low in strategic Elements", *Metallwirtschaft*, 23, 14–2, (1944).
6. Linley A., "Substitute High-Speed Steel", *J. Birmingham Met. Soc.*, 24, 3–27 (1944).
7. Kalpers, H. "High Speed Steels", *Automobiltech Z.*, 45, 582–5 (1942); *Chem. Zentr.*, I, 1211, (1943).
8. Oliver, Frank J., "Tipped High Speed Steel", *Iron Age*, 58–61, 137–139 (Jan. 18, 1945).

General References:

Breeler, W. R., "Development in Molybdenum High-Speed Cutting Steels", *Trans. Amer. Soc. for Metals* (Oct. 1937).

Emmons, J. V., "Some Molybdenum High Speed Steels", *Trans. Am. Soc. for Steel Treating, XXI*, No. 3, 193-232 (Mar. 1933).

Garratt, Frank, "New High Speed Steel", *Metal Progress*, 38-43 (June, 1935).

Kennedy, R. G., "The Microstructures of Mo-Max and 18-4-1", *Metals and Alloys*, 289-293 (Oct. 1937).

Ritchie, S. B., "Molybdenum in High-Speed Steel", *Army Ordnance XI*, No. 61, 12-19 (July-August, 1930).

Anon., "High-Speed Steels Low in Tungsten", *Supplement to the Engineer*, 101-2 (Feb. 25, 1938).

Anon., "New High-Speed Steels", *Metal Progress*, 492-3 (May, 1939).

Chapter IX

The Economics of Tungsten

In regard to the economics of tungsten, statistics of the industry throw considerable light on the future trend of production and of price, as well as on certain implications regarding economic competition among the principal producing countries. But statistics *per se*, as they are generally recorded in publications, are often confusing, so much so that after having plodded through a labyrinth of figures, one is not always able to arrive at any conclusion of real value. One must try to read meanings into the figures; and in order to do that it is necessary to discern certain patterns in them. Inasmuch as tungsten enters principally into the manufacture of tool steels, cycles can be discerned in its production and its price. These will be called periods, instead of cycles, because there are forces at work which bring out definite patterns in the productions and prices of tungsten despite their apparent irregularity.

As shown in Tables 1 and 4, the production and prices of tungsten, from 1913 to 1937 inclusive, can be grouped into six periods: 1. Pre-War Period (1913–1914), 2. War Boom Period (1915–1918), 3. Post-War Reaction Period (1919–1925), 4. Revival Period (1926–1929), 5. Depression Period (1930–1934) and 6. Re-Armament Period (1934–1937).

This discussion does not include the present period, that is, from 1938 to the present because, on account of the present world turmoil, statistics of the production of some countries like Burma are unavailable, and transportation difficulties have prevented the normal flow of production of some important countries, such as China, into the world market.

China, starting in the Pre-War Period with a production amounting almost to nothing, had been climbing up to about 85 per cent during the Revival Period, but came down to about 40 per cent during the Re-Armament Period, the average production during the last twenty-five years being 37 per cent of world production. As to Burma, its production during the Re-Armament Period was about 5 per cent less than that during the Pre-War Period with respect to world production, being 24 per cent for the former and 19 per cent for the latter, averaging 17.4 per cent for the six periods taken together. When we take the average yearly production of Burma from 1919 to 1933 as 1800 tons and that from 1934 to 1937 as 4500 tons, we find the ratio between the former and latter production to be

TABLE 1.—World Production of Tungsten Concentrates
(M. T. containing 60% WO_3)

Name of Period	Period	China	Burma	U. S.	Bolivia	Malaya	Portugal	Japan	Australia	Argentina	Indo-China	Spain	Siam	Great Britain	Total	Av. Yearly Production (World)
Pre-War Period	1913–1914		3.738	2,292	587	822	1,793	461	1.572	1,012	289	304	553	419	15.550	7,770
War Boom Period	1915–1918	12,082	14,450	17,654	12,005	4,047	5,101	5,152	4.614	2,722	1,487	1.594	1.919	1,329	89.673	22,400
Post-War Reaction Period	1919–1925	28,556	10.941	2,305	3,192	3,455	2,576	960	2,348	848	1,600	580	471	349	60,458	8,630
Revival Period	1926–1929	31,916	5,238	4,159	1.847	1,182	1,041	364	764	108	714	702	80	154	48,961	12,240
Depression Period	1930–1933	25,195	10,455	3,082	2,224	3,767	1,403	426	535	134	965	478	19	288	49.300	12,300
Re-armament Period	1934–1937	39,992	19,154	9,577	5,760	7,317	5,077	3,424	2,099	2.404	1.867	49	200	840	98,550	24,600
Total	1913–1937	134,141	63,067	39,067	25.605	20,590	16.991	12,600	11,932	7.218	6,922	3,900	3.900	3,395	362,492	14,000
Percentage		37.0	17.4	10.8	7.0	5.7	4.7	3.5	3.3	2.0	1.9	1.1	0.9	0.9	100	Av. of 25 years

TABLE 2.—World Production of Tungsten Concentrates in Percentages

Name of Period	Period	China	Burma	U. S.	Bolivia	Malaya	Portugal	Japan	Australia	Argentina	Indo-China	Spain	Siam	Great Britain
Pre-War Period	1913–1914		24.0	14.7	3.8	5.3	11.5	3.0	10.1	6.5	1.8	1.9	3.6	2.7
War Boom Period	1915–1918	13.5	16.1	19.7	13.4	4.5	5.7	5.75	5.1	3.0	1.6	1.8	2.1	1.5
Post-War Reaction Period	1919–1925	47.2	18.1	3.7	5.3	5.7	4.3	1.6	3.9	1.4	2.6	0.96	0.8	0.6
Revival Period	1926–1929	65.1	10.7	8.5	3.8	2.4	2.1	0.74	1.6	0.2	1.5	1.4	0.16	0.31
Depression Period	1930–1933	51.1	21.2	6.3	4.5	7.6	2.8	0.86	1.1	0.25	1.96	0.97	0.04	0.5
Re-armament Period	1934–1937	40.6	19.5	9.7	5.9	7.4	5.1	3.5	4.2	2.1	1.9	0.05	2.0	0.85

World Production of Tungsten Concentrates (1895–1905)* in M.T.

	1895	1896	1897	1898	1899	1900	1901	1902	1903	1904	1905
Australia	35	30	35	105	535	280	85	65	250	1645	1790
Queensland	25	3	13	79	263	193	73	56	200	1564	1450
United States	—	—	—	78.8	201.6	264	214.8	184 265	292	375	750
Colorado	—	—	—	45.5	—	45.5	65	—	—	148	540 630
South America (Argentina, Chile, Bolivia, Brazil)	—	—	—	—	—	About 125	—	—	—	About 30	About 50
Spain	31	14	10	37	151	1958	6	11	—	60	900
Portugal	12	14	29	59	55	49	90	234	228	358	—
Germany	—	41	38	50	50	43	43	31	35	34	34
Austria	—	36	31	36	36	50	45	—	—	—	—
Great Britain	—	44	127	331	96	9	21	9	276	164	174
	103	182	283	821.3	1387.6	2986.5	642.8	671	1281	4378	5778

---

* Leiser, Heinrich, "Wolfram", Verlag von Wihelm Knapp, Hall a.s, p. 26, 1910.

TABLE 3.—Available Supply of Tungsten In the U. S. (In Thousands of lbs of Metallic Tungsten)

Name of Period	Period	Av. Yearly Domestic Production	Av. Yearly Available Supply	% of Supply Produced in U. S.	% of World Output		Total World Production in Yearly Average
					Produced in U. S.	Consumed in U. S.	
I. Pre-War Period	1913–1914	1,200	2,610	46	16	32	8,150
II. War Boom Period	1915–1918	4,630	9,400	50	20	40	23,600
III. Post War Period	1919–1925	350	3,400	16	3.8	38	9,000
IV. Revival Period	1926–1929	1,090	4,700	23	8.5	37	12,800
V. Depression Period	1930–1933	800	1,660	50	6.1	12.8	12,970
VI. Re-armament Period	1934–1937	2,500	5,200	50	10	20	25,900
Average	25 year Period	1,600	4,520	35.5	10	30	15,240

TABLE 4.—Average Yearly Production of Tungsten Concentrates (M. T. containing 60% WO_3)

Name of Period	Year	Average Price	China	Burma	U. S.	Bolivia
I. Pre-War Period	1913–1914	32s *(27–55)		1,860	1,140	290
II. War Boom Period	1915–1918	54s *(29–60)	3,020	3,800	4,410	3,000
III. Post War Reaction Period	1919–1925	19s *(9–55)	4,080	1,590	330	450
IV. Revival Period	1926–1929	19s *(12–40)	8,000	1,300	1,040	460
V. Depression Period	1930–1933	16f *(10–33)	6,290	2,600	770	550
VI. Re-armament Period	1934–1937	46s *(25–130)	9,990	4,800	2,400	1,440
Recent	**1937–1942 (figures approximate)**		**65,000**	**30,000**	**42,000**	**29,000**

*** These figures represent the minimum and maximum prices of each period.**

TABLE 5.—World Production of Tungsten Concentrates
(M. T. containing 60% WO_3)

Year	China	Burma	United States	Bolivia	Malaya	Portugal	Japan	New Zealand	Australia	Argentina	Indo-China	Spain	Siam	Great Britain	Mexico	Peru	Sweden	Africa‡	Brazil	Canada	Total*
1905			303	75		320			1,940			413		193							3,479
1906			928	75	151	629			1,387	326		222	10	304							4,320
1907			1,640	600	89	702			1,378	507		303		361							6,161
1908			671	187	83	684			833	548		249		261							3,898
1909			1,469	152		554	265		1,009	817		129									4,777
1910			1,655	210		1,030	250		1,414	751		153									6,125
1911			1,035	336		980	261		1,147	621		96									5,812
1912			1,210	497		1,330	205		1,131	638		150									7,470
1913		1,572	1,394	297	362	1,126	257		848	575	127	169	280	197							8,123
1914		2,166	898	290	460	667	204		724	437	162	135	273	222							7,427
1915	35	2,464	2,116	859	488	953	456		889	169	333	189	432	360							10,866
1916	109	3,510	5,373	3,228	841	1,418	1,285		1,052	854	343	425	530	407							21,046
1917	1,361	4,294	5,574	4,215	1,171	1,580	1,682		1,306	1,085	433	446	726	255							25,819
1918	10,577	4,182	4,591	3,703	1,547	1,150	1,729		1,367	614	378	534	231	307							31,942
1919	2,654	3,624	297	2,161	1,288	706	771		1,249	204	284	302	258	177							14,744
1920	4,712	2,983	196	766	553	237	175		624	182	284	57	137	83							11,494
1921	2,657	673		174	72	306			17	52	452	25	76	81							4,836
1922	3,873	1,038		9	372	527	14		44	125	112			3							6,221
1923	4,554	960	219		434	289			119	144	129	9		2							6,953
1924	3,398	814	513		321	304			75	137	150	161		2							6,159
1925	6,708	849	1,080	82	425	207			220	4	189	26		1							10,051
1926	7,989	1,634	1,254	109	333	358	19		99	11	92	123	10	20							12,231
1927	5,666	1,277	1,056	79	192	174	54		179	10	213	164	8	12							9,282
1928	8,283	843	1,096	29	144	151	215		238	24	211	158		95							11,648
1929	9,978	1,484	753	1,630	513	358	76		248	63	198	257	62	27							15,800
1930	9,454	2,699	637	888	1,232	499	94		241	98	220	254	7	153							16,700
1931	7,492	2,474	1,274	410	703	274	73		94	20	248	135	12	121							13,400
1932	2,249	2,226	359	686	553	272	84		50	6	247	43		2							6,800
1933	6,000	3,056	812	240	1,279	358	175		150		250	46	36	12							12,400
1934	5,099	3,913	1,859	794	2,011	610	469		419	392	300	49	82	223							16,450
1935	7,998	4,527	2,173	1,423	2,035	1,140	1,045		491	579	417	?	82	256							22,500
1936	7,638	5,299	2,370	1,741	2,037	1,379	1,910		426	702	503	?	82	221							24,800
1937	17,895	5,924	3,175	1,802	1,356	2,069	2,100		894	866	648	?	221	148	33	30	127	562	6		37,800
1938	13,387	6,334	2,761	2,530	1,082	2,810	2,000?		1,239	1,195	545	500	251	258	76	170	180	700	2		36,000
1939	11,580	7,400	3,889	3,337	608	3,851	2,000?		1,100?	1,309	510	500	378	250?	118	170	200	800	7	4	38,000

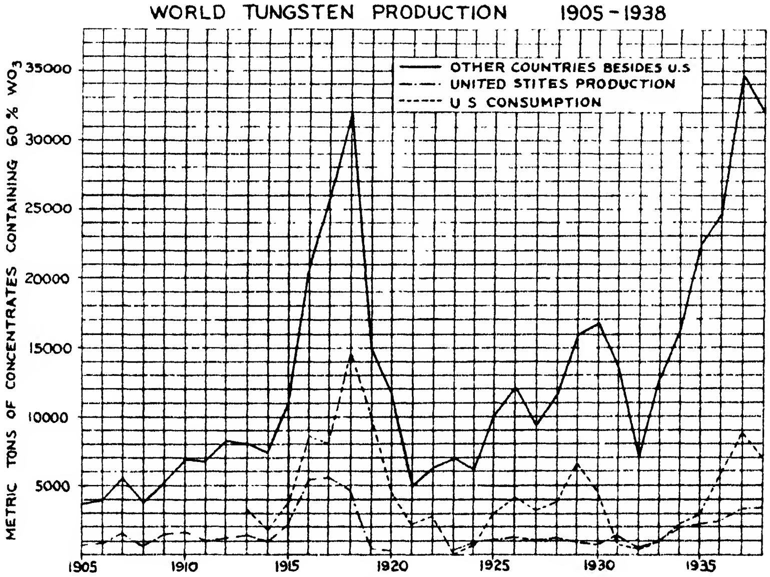
1940	14,500	9,000	4,825	4,183	535	4,858	2,000?		1,200?	1,560	392	500	200?	250?	112	290	200?	770	9	6	44,600
1941	9,300	8,300	6,500	5,100	500	5,500	2,000?		450	1,900	500	600	500	100?	170	245	200?	900	35	32	47,000
1942	10,000†	5,000?	9,453	4,904	375?	3,100	2,000?		150	1,763	505	900	500	58	193	187		1,360	15	244	
1943	10,000†	5,000?	12,055	5,991	375?	3,500	2,000?	100	270	2,104	500	2,900	610	74	516	522		1,130	1,151	798	
1944	8,000†	5,000?	10,259	8,660	375?	7,090	2,000?	125	500	2,241	510	3,018	590	125	336	655		405	1,969	466	
1945	7,000†	5,000?	5,807	6,164	375?	3,520	2,000?	280	530	1,105	450	1,560	550	120		850			2,528		
1913-1937																					
Totals	134,141	63,976	39,067	25,605	20,590	16,991	12,600		11,932	7,218	6,922	3,900	3,300	3,395							362,600
Per cent	37.0	17.4	10.8	7.0	5.7	4.7	3.5		3.3	2.0	1.9	1.1	0.9	0.9							100.0

* Includes minor outputs from countries not listed.

† Figures are roughly calculated from the shipments made to U. S. A. and Russia.

‡ Mainly from Belgian Congo and Union of South Africa.

1 to 2.3 which, it is significant to note, is almost identical with the price ratio of 1 to 2.5, taking 18s as the average price from 1919 to 1933 and 46s as the average price from 1934 to 1937. Again, almost the same can be said with regard to the increase in Bolivian production during the above-mentioned periods of years. Bolivia produced 7 per cent of the world production during the last twenty-five years. The United States, during the War Boom Period, produced about 20 per cent of the world production, but during the Re-Armament Period the percentage dropped to about 10 per cent, which is also the average for the last twenty-five years.



[Graph showing relative importance of tungsten production: world and United States. *After J. F. Partridge, Jr. (modified).*

Of principal tungsten-consuming countries, the United States is in a unique position, in that she is both a producer and a consumer, while Great Britain and Germany have to depend entirely upon import. During the last twenty-five years the United States produced 10 per cent and consumed 30 per cent of the world production; that is, she had on an average to import 20 per cent of the world output, as shown in Table 3. But, in fact, during the Re-Armament Period, she only imported 10 per cent of the world output, the reason being that during this period it was mainly Germany and Great Britain, and to a certain extent France and Italy who raced for re-armament. It has been estimated that during 1936 Germany imported 35 per cent, Great Britain 36 per cent and the United States 12 per cent, aggregating 83 per cent of the world output.

While the average yearly world production during the last twenty-five years was 14,000 tons, during the War Boom Period and the Re-Armament Period the yearly production amounted to an increase of 50 per cent of the average world production, and this increase coincided with the increase in price in nearly the same proportionate amount; that is, the average of the price of the War Boom Period and the Re-Armament Period amounted to an increase of about 50 per cent of the average prices of the twenty-five years.

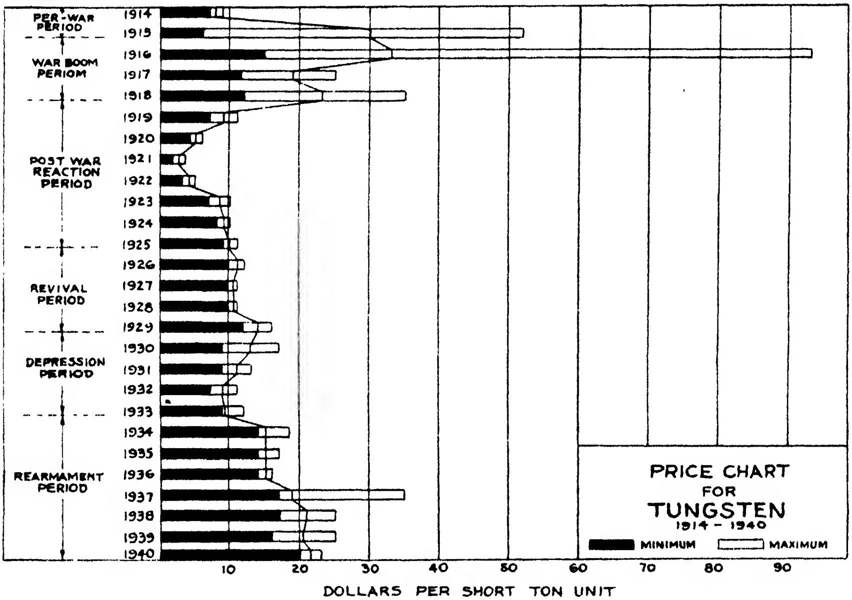


Chart indicating fluctuations in the price of tungsten. *After J. F. Partridge, Jr. (modified).*

The World Tungsten Production during 1942–1944

Due to the exigencies of the War and the blockading of the pre-war regions of production, the center of tungsten production has been shifted from the East to the West. Whereas before the War China, Burma and the Malaysian regions furnished about sixty five per cent of the world requirement, their production now toward the war effort of the Allied Nations has been neglibible. What has met with the requirement of the War now has come mostly from the United States, Bolivia, Brazil, Canada, Spain and Portugal, and Australasia.

The United States. Production, short tons of 60 per cent WO_3

1942	9,433
1943	12,045
1944	10,500 (estimated)

Bolivia. Production, metric tons of 65 per cent WO_3

1943	4,141
1944	(by July exports had dropped to 32 tons for that month)

Brazil. Production, metric tons of 70 (?) WO_3

1942	150
1943	1,551
1944	1,608

Portugal and Spain. The yearly production during this period may be more than 6,000 tons from the former and 1,000 tons from the latter. The "preclusive buying" policy of the Allied Nations to keep Germany from obtaining this war-valuable product rendered it necessary for the United States to pay $50 a unit and in some instances as high as $100 a unit.

Prices

The high price of wolfram prevailing in 1937, being on an average 69s 10¼d per unit, had so induced increased production in countries other than China and Burma, that the price in 1938 dropped to 56s 2¾d, the average of that year. Contrariwise, consumption in 1938, as against that in 1937, had not maintained the same pace as the increased production in 1938 compared with that in 1937. For instance, the net import of wolfram into Great Britain by the Murex, Ltd., and the High Speed Steel Alloys Company, amounted to only 6,758 tons in 1938, while in 1937 it was 8,670 tons.

A glance at the movement of prices of wolfram from 1909 to 1939 would reveal the following salient points:

1. Before World War I, from 1909 to 1914, the average price per unit was about 32s, which may be considered quite normal for that period.
2. During that war, from 1915 to 1918, the price, arbitrarily fixed for a certain time by the British Government, was 60s per unit. This period may be called the War Boom Period. The average price during this period was 54s per unit.
3. Following it, from 1919 to 1925, the price gradually fell to a low point of 9s in 1922. The average price of this period may be regarded as 19s. The adversity of the wolfram market during this period was due to the

logical consequence following the First World War and may be considered exceptionally abnormal in the range of years under consideration. This period may be called the "Post War Reaction Period".

4. From 1926 to 1929 prices for all metals had shown a decided improvement. With regard to wolfram, the price rose the latter part of 1927 from 12s, the lowest during this period, to 40s, the highest during this period, in the middle of 1929. This period may be called the "Revival Period", the average price of which was 19s.

5. From 1930 to 1933, the world was in the grip of depression. Consequently, the price dropped in the first part of 1933 to 10s, even with "paper sterling", as England had meanwhile given up the gold standard. This period may be called the "Depression Period", during which the average price was 16s.

6. From 1934 to 1937, business gradually improved while the European Powers were racing for rearmament. The price jumped from 25s in the middle part of 1936 to an unprecedented height of 130s the latter part of 1937. This period may be called the "Re-Armament Period", and its average price was 46s.

In a word, if the average of the average prices of the six periods are taken, 32s per unit will be arrived at as the average of the price from 1909 to 1937, which corresponds approximately to two-thirds of the average price of the War Boom Period and the Re-Armament Period, as already noted.

Again, upon averaging the averages of the six peak and bottom prices during the last thirty years, a price of 41s can be arrived at thus:

	Peak prices	
last quarter 1909	55s	
1917–1918	60s	
first quarter 1926	25s	
third quarter 1929	20s	
middle of 1934	50s	
last quarter 1937	130s	
	360s	divided by 6 = 60s

	Bottom prices	
middle of 1914	27s	
second quarter 1922	9s	
third quarter 1927	12s	
second quarter 1933	10s	
middle of 1936	25s	
end of 1939	30s	
	133s	divided by 6 = 22s

Hence the average of the above is 41s.

It should be noted here that price fluctuation of tungsten ore is more violent than that of antimony. During the last twenty-five years, the highest price of tungsten ore was fourteen times the lowest price, while that of antimony was nine times the lowest price.

Tungsten Ore Prices in the United States in Dollars per Short Ton Unit of WO_3 in 60 per cent concentrates, including duty

Year	Average Quoted Price	Year	Average Quoted Price
1900	2.75	1921	3.15
1901	2.58	1922*	4.02
1902	2.75	1923	8.33
1903	2.49	1924	8.51
1904	2.25	1925	11.07
1905	5.57	1926	11.23
1906	6.26	1927	10.70
1907	9.04	1928	10.81
1908	5.71	1929	14.76
1909	6.32	1930*	13.40
1910	7.68	1931	11.45
1911	5.97	1932	10.51
1912	6.27	1933	11.36
1913	7.24	1934	16.70
1914	7.32	1935	16.00
1915	29.30	1936	15.46
1916	33.98	1937	21.79
1917	30.85	1938	20.61
1918	22.27	1939	20.43
1919	8.69	1940	23.44
1920	7.26	1941	25.00

1942	24	Under government control
1943	24	
1944	24	
1945	24	

Tungsten Ore Prices in Europe in Shillings Per Long Ton Unit of WO_3

Year	Min.	Max.	Year	Min.	Max.
1909	22	55	1924	10	12
1910	35	48	1925	12	24
1911	28	36	1926	13	25
1912	28	35	1927	12	17
1913	29	35	1928	14	21
1914	27	29	1929	18	40
1915	29	55	1930	15	34
1916	55	55	1931	12	15
1917	55	60	1932	11	15.5
1918	60	60	1933	10	29
1919	30	60	1934	28	50
1920	21	35	1935	29.5	39
1921	11	20	1936	25	35
1922	9	14	1937	33	130
1923	12	14	1938	58	90
			1939	50	58

1940	50	Under government control
1941	50	
1942	55–100	
1943	55–100	
1944	55–100	
1945	75– 90	

---

* See section on "The American Tariff," p. 381.

European Ferro-Tungsten Market

The market for ferro-tungsten in Europe up to 1938 can be broadly divided into three regional groups. They are: (1) the International Ferro-Tungsten Convention whose members are England, France, and Germany; (2) the "neutral" countries; and (3) Soviet Russia.

The three countries—England, France, Germany—compose the first group because, first, the producers in these countries have joined together to form the International Ferro-Tungsten Convention; secondly, because the policies of the three Governments have an identical purpose of protecting their own respective manufacturers; and thirdly, because the producers command a strong position in the world market.

The important objects are, first, to regulate sales between the groups; secondly, to regulate competition and profit-sharing from sales in the "neutral" countries; and thirdly, to decide on matters covering purchases, supplies of ores, etc.

The English group consists of the High Steel Alloys Ltd., of Ditton Road, Widnes, and Murex Ltd., of Rainham (Essex).

The members of the French group are:

Société d'Electrochimie, d'Electrométallurgie et des Acieries Electriques d'Ugine, 10 Rue du Général Foy, Paris (8eme).
Société Electro-Métallurgique de Saint Beron 101 Rue de l'Hotel de Ville, Lyon (Rhone). Société Electro-Métallurgique de Montricher, 66 Rue de la Chaussee d'Antin, Paris (9eme).

The members of the German group are:

Gesellschaft Für Elektrometallurgie M.B.H., Dr. Paul Grünfeld, Hardenbergstrasse, 3 Berlin-Charlottenburg, 2.
I. G. Farbenindustrie Aktiengesellschaft, Verkausgemienschaft Chemikalien, Abteilung M III, Gruneburgplatz, Frankfurt a. Main (20), and Hermann C. Starck A. G., Tauentzienstrasse 12B, Berlin W. 50.

The Convention has been successful in their operation principally because of Government support and protection. An equally important factor is the huge financial resources which the member firms command, and the wide ramifications of interests which they control in their own countries as well as in other parts of the world. Following is a closer examination of these two factors:

The English Government levies an import duty of 33⅓ per cent *ad valorem* on ferro-tungsten under the Key Industry Duties Act. The import duty in Germany is R. M. 25 per 100 kilos for materials containing 20 per cent and upwards of tungsten in alloy, and in addition imports are subject to licenses owing to the strict foreign-exchange regulations. The import duty into France on ferro-tungsten apparently varies according to the country of origin, the minimum rate being 12.8 per cent *ad valorem* and the maximum 51.2 per cent *ad valorem*, and in each case there is an additional duty of 14 per cent on the duty levied. These duties or import licenses may be subject to immediate increase or change. Tungsten ore, however, is admitted free of duty, with the exception of France, which levies a sales tax of 8 per cent *ad valorem*.

As to the sources of supply for tungsten in times of peace, England was rather favorably situated. She drew from her colonies—Nigeria, South West Africa, Southern Rhodesia, Tanganyika Territory, Union of South Africa, India, Burma, Federated Malay States, Unfederated Malay States, Australia, and New Zealand. Other sources available are Portugal, Spain, Bolivia, etc. Though France was not so well situated as England, she still has a source in French Indo-China. Germany is the least favorably situated.

The countries in the second group are: Austria, Poland, Czechoslovakia, the Balkan States, Scandinavian countries, Belgium, Holland, Denmark, and Italy. They are classified as "neutral" countries because they have no high protective tariff for ferro-tungsten, and the market there for this alloy is free and open.

Italy is an exception. She prohibits the importation of ferro-tungsten. She has her own conversion facilities. She executed some conversion orders for account of Russia.

Russia is the third group. She imported 1,878 long tons in 1936, and 848 long tons in 1937. These figures show a considerable drop in the imports of ferro-tungsten. It is interesting to note, on the other hand, that in 1936 she imported 1,030 long tons of ferro-molybdenum, and in 1937 she increased the amount to 1,387 long tons. While the figures cannot conclusively show any tendency, still we may well ask, can the decrease in the import of ferro-tungsten be due to the establishment of their own conversion facilities, or to the shift of using more ferro-molybdenum to replace ferro-tungsten?

Import Duties of Ferro-Tungsten

United Kingdom

Dutiable under Key Industry Act 33⅓ per cent *ad valorem*.

Germany

For material containing 20 per cent and upward of tungsten in alloy the duty is R.M. 25 per 100 kilos, and in addition, of course, all imports into Germany are subject to license owing to the strict foreign-exchange regulations ruling in that country.

France

The import duty into France apparently varies according to the country of origin, the minimum rate being 12.8 per cent *ad valorem* and the maximum 51.2 per cent *ad valorem*. In each case there is an additional duty of 14 per cent of the duty levied.

Belgium

The import duty is 70 c. per 100 kilos of alloy.

Italy

For an alloy containing more than 5 per cent of tungsten the full rate is 105.7 lire per 100 kilos and the Convention rate is 79.3 lire per 100 kilos.

Sweden

The import duty on ferro-tungsten is 35 kronen per 100 kilos.

It is interesting to note that all the countries mentioned above allow the import of tungsten ore free of duty, except that in the case of France, Belgium and Italy universal taxes on all imports are levied. For instance, in France there is a sales tax of 8 per cent *ad valorem*, in Belgium a transmission tax of 2½ per cent *ad valorem* and in Italy a sales tax of 2½ per cent *ad valorem*.

Price of Ferro-tungsten

	Per lb of W contained 75 to 80 per cent W f.o.b. works		Per lb of W contained 75 to 80 per cent W f.o.b. works
1929	$1.05	1935	$1.40
1930	1.40	1936	1.35
1931	1.10	1937	1.75
1932	1.00	1938	1.80
1933	.95	1939	1.90
1934	1.30	1940 (Jan.–Feb.)	2.00

Specifications for Ferro-tungsten

A proposed tentative specification of the American Society for Testing Materials[1] for ferro-tungsten states that the material shall be furnished crushed to a size of 1 in or less and shall conform to the following requirements as to chemical composition:

	Percentage, as Specified		Percentage, as Specified
Tungsten	75.00 to 85.00	Copper, max.	0.15
Carbon, max.	0.75	Arsenic, max.	0.10
Phosphorus, max.	0.06	Antimony, max.	0.08
Sulfur, max.	0.06	Tin, max.	0.10
Silicon, max.	1.00	Sum of As, Sb, and Sn, max.	0.20
Manganese, max.	1.00		

A recent specification for ferro-tungsten, according to the Electro Metallurgical Sales Corporation (a unit of Union Carbide and Carbon Chemicals Corporation), is as follows:

	Percentage		Percentage
Tungsten	78.00 to 82.00	Arsenic	0.05 max.
Manganese	0.75	Antimony	Not to exceed 0.05
Silicon	0.50	Bismuth	Not to exceed 0.05
Carbon	Up to 1.00	Sulfur	0.05 max.
Phosphorus	0.05 max.	Molybdenum	0.25 max.
Copper	0.05 max.	Tin	0.05 max.

Specifications of Tungsten Concentrates in the United States

Government Specifications of Tungsten Ore

Scheelite (%)		Wolframite (%)
60.00	WO_3	65.00
0.10	Sn	1.50
0.05	Cu	0.05
0.05	P	0.05
0.10	As	0.25
0.10	Sb	0.10
0.25	Bi	1.00
0.40	Mo	0.40
0.75	S	0.50
1.00	Mn	

Standard Specifications of the Trade

Scheelite (%)		Wolframite (%)
60.00 to 70.00	WO_3	65.00 to 70.00
none to 0.10	Sn	1.00 to 1.50
none to 0.10	Cu	none to 0.10
0.05 to 0.10	P	0.05 to 0.10
trace to 0.10	As	0.10 to 0.25
trace to 0.05	Sb	none to 0.50
0.05 to 1.00	Bi	none to 1.00
0.05 to 0.40	Mo	0.04 to 0.40
none to 0.50	S	0.10 to 0.50
none to 1.00	Mn	none

Characteristics of Tungsten Ores of Different Countries

It is scarcely possible to state which country produces originally the best quality of tungsten ore and which country does not. What can be stated is that the country with the superior facilities in man power, water power, chemicals, machinery and engineering can produce better tungsten concentrates than those countries which lack such facilities. In general, the quality of tungsten ores as produced in the different parts of the world is irregular; however, outcrop ore is as a rule comparatively pure, as is evidenced in the tungsten deposits in China. The characteristics of tungsten ores, particularly their objectionable impurities, by countries, are as follows:

China. The Chinese ore is predominantly wolframite, with a small quantity of hübnerite, ferberite and still less of scheelite. There is, however, a considerable quantity of Chinese ore which may be called wolfram-scheelite, with scheelite running from 15 to 30 per cent. There is also a considerable quantity of tinny wolframite or tinny wolfram-scheelite, a typical analysis of which is as follows:

Wolfram-Scheelite	
WO_3	69.28%
Sn	2.66
As	0.25
Cu	0.05
S	0.36
P	0.02
Mo	0.04
Bi	0.32
Sb	trace

Tinny Wolfram-Scheelite	
WO_3	38.40%
Sn	0.72%
As	0.72%
Cu	0.08%
S	1.20%
P	0.03
Mo	0.06
Bi	0.55%
Sb	0.21%

U. S. A. The United States production consists mostly of scheelite, with some ferberite and still less hübnerite. With the facilities in America most concentrates which come to the market are rather good and are capable of meeting standard specifications, with the exception of the ore from Pine Creek, Bishop, California, which is a mixture of scheelite and molybdenite, necessitating first their separation and then the purification of the scheelite, by means of power metallurgy. The largest single scheelite deposit in the United States is at Stibnite, Idaho. This scheelite deposit, because of its close association with antimony sulfide and apatite, carries a considerable percentage of antimony and phosphorus even after concentration.

The tungsten-manganese ore as mined at Golconda, Nevada, cannot be separated by gravity or flotation and has to be treated chemically.

Bolivia. There has been some exceptionally pure tungsten ore coming from Bolivia in large crystals and practically free from impurities. Due to the lack of facilities, however, most of the Bolivian ore reaching the world market requires further treatment before it can be used by consumers. This treatment is for the removal of either Sn, As, S, P, Mo or Cu. Besides the regular ore, Bolivia produces two unusual ores which may be described as follows:

Barite Scheelite Ore: A typical analysis is:

WO_3	33.57%
BaO	22.50
P	0.04
S	6.94

Since the specific gravity of barite (4.3 to 4.6) is not much different from that of scheelite (−5.9 to 6.1), mechanical separation is difficult. No suitable agent has been found to make a differential flotation separation. It is not the barium oxide that is objectionable to the consumers so much as the high percentage of sulfur, whose limit is 0.50 per cent in the Standard Specifications.

Tinny Wolframite-Ferberite-Scheelite Ore: A typical analysis is:

WO_3	22.94%
Sn	24.82
As	1.85
P	.13
S	14.14
Cu	.07
Bi	.57
CaO	4.92

Such ore can only be treated successfully by both chemical and mechanical means. There seems to be a large quantity of this ore in Bolivia.

Argentina. Argentina tungsten ore consists of both wolframite and scheelite mixed in variable proportions. The so-called wolframite ore contains generally about 10 to 15 per cent of scheelite, and the so-called scheelite contains 6 to 10 per cent of wolframite. Most of the Argentine ores, regardless of whether they are wolframite or scheelite, are generally high in P and Cu, sometimes 3 to 5 times more than the standard specifications call for. Further treatment is required in order to lower the P and Cu content. There is also one bismuth tungsten deposit in Argentina, with tungsten about 55 per cent and bismuth about 14 per cent.

Peru. Peru does not produce scheelite; all her production is wolframite. The Peruvian ores are generally high in As, S, and Cu.

Brazil. The Brazilian tungsten ore is mostly in the form of scheelite. Its chief impurity is Mo which is sometimes as high as 2 per cent.

Mexico. Mexican production of tungsten is generally in the form of scheelite, although ferberite occurs in one or two deposits. The Mexican scheelite in its virgin stage is generally high in Cu, P, S, and Mo, which by treatment can be made to conform to standard specifications without much difficulty. Typical assay of Mexican scheelite is as follows:

WO_3	45 to 62%
P	0.15 to 0.30
S	2.04 to 0.6
Cu	0.65 to 0.7
Mo	1.0 to 1.5

South Africa. South Africa produces both scheelite and wolframite. The scheelite from the Union of South Africa is generally high in Mo and that from Rhodesia is high in Cu. The wolframite from South Africa is high in S, and Cu, and sometimes in Sn.

Malay Straits. Malay Straits produce a very high-grade scheelite with very little impurities, WO_3 being sometimes as high as 78 per cent.

Burma. Burma, like China, produces two kinds of tungsten ore; one is of high grade corresponding to that of the Chinese; the other is the tinny wolframite which is similar to the Chinese tinny wolframite. The tungsten production in the form tinny wolframite in Burma is considerably larger than that of the high-grade wolframite.

Thailand. Up to the present, Thailand has produced only wolframite. After treatment for the elimination of sulfur, the ore is then regarded as satisfactory.

Indo-China. Indo-Chinese ore is similar in characteristics to that of China.

Portugal and Spain. Portuguese and Spanish ore is mostly a mixture of ferberite and wolframite, with occasionally a little scheelite. Its general impurities are P, S, and Cu. A typical assay of such ore is as follows:

WO_3	64.65%
P	0.11
S	1.02
Cu	1.07

Marketing of Tungsten Ore

Tungsten ore is sold on the basis of so much per unit. In the United Kingdom and British Colonies, except Canada, the unit is 22.4 lbs, and it is sold at so many shillings per unit of long ton (2240 lbs). In China, Germany and France the unit is 22.04 lbs, and it is sold at so much per unit of metric ton (2204 lbs). In the United States and Canada the unit is 20 lbs and it is sold at so many dollars per unit of short ton (2000 lbs).

Chinese tungsten ore is sold in Europe generally under a contract known as the "Hamburg Contract A" (See Appendix II). Other ores are sold under "Contract B" (See Appendix II). In the United States there are standard specifications, but no standard contract. The American consumers have their own specifications and therefore buy their ore according to their own specifications. The Army and Navy and the Metals Reserve Company have their own specifications.

The American Tariff

Tungsten as a raw material was imported into the United States free of duty until September 20, 1922 when duty was imposed at the rate of 45 cents per pound of W content or $7.14 per unit of WO_3 short ton (2000 lbs). This is known as the Act of HR-7456. This import duty remained the same until June 18, 1930, when the Smoot-Hawley Tariff Act was passed, providing for a duty of 50 cents per pound of W, or $7.93 per unit of WO_3. It is admittedly a protective tariff for the tungsten mining industry in the United States.

The tariff rates for tungsten products under the Smoot-Hawley Act of 1930, paragraphs 301, 302 and 316 are as follows:

Tungsten, alloys of, nspf	60¢ lb on tungsten contained therein and 25%
" carbide, and mixtures or combination containing tungsten carbide, in lump, grain or powder	60¢ lb on tungsten contained therein and 50%
" compounds of	60¢ lb on tungsten contained therein and 40%
" concentrates	50¢ lb on the metallic tungsten contained therein
" metal and mixtures or combinations containing tungsten metal, in lumps, grains or powder	60¢ lb on tungsten contained therein and 50%
" nickel	60¢ lb on tungsten contained therein and 25%
" ore or concentrates	on the metallic tungsten contained therein, 50¢ lb
" steel scrap containing 14% of tungsten as scrap steel, TD 42112	75¢ ton and on tungsten content in excess of 2-10 of 1%, 72¢ lb
" wire, steel wire containing over 2-10 of 1% of tungsten, 25% p. 316 and 8% p. 305, CIE 4126 3-15-27	

Apparent Consumption by Countries of Tungsten by the Principal Users of the Metal[2]

Country	Consumption (Reduced to equivalent of 60 per cent, tungstic oxide, WO_3) In Metric Tons				Per cent of Consumption by Countries Listed			
	1934	1936	1937	1938	1934	1936	1937	1938
Germany	4,700	10,060	13,000	16,340	27.0	38.3	41.0	60.5
United Kingdom	3,900	10,260	10,100	7,750	22.4	39.3	31.9	28.7
United States	3,020	5,850	8,580	2,910	17.5	22.4	27.1	10.8
Begium-Luxemburg	2,100				12.1			
France	1,800				10.3			
U. S. S. R.	800				4.6			
Japan	1,070				6.1			

References

1. Hoffman, N. B., Chairman, Report of Committee A-9 on Ferro-alloys, *Proc. Am. Soc. Test. Mat.*, **32**, part 1, 134-135 (1932).
2. Stevenson, John S., Bulletin No. 10 (Revised) British Columbia Dept. of Mines, p. 38 (1943).

General:

Brown, J. C., "Notes on Wolfram", *Bull. of Indian Industries and Labour*, No. 7, Government Printing, India, 1921.

Emeny, B., "The Strategy of Raw Materials", pp. 76-84 (Macmillan & Co.), New York, 1936.

Hardy, C., "Marketing Tungsten Ores", *Eng. and Min. Journ-Press*, 666-669 (April 22, 1922).

Roush, G. A., "Strategic Mineral Supplies," 130-161 (McGraw-Hill Book Company) New York, 1939.

"The Mineral Industry" (McGraw-Hill Book Co.), Annual volumes.

"Minerals Year Book", U. S. Bureau of Mines. Annual volumes.

"The Marketing of Tungsten Ores and Concentrates", *Trade Information Bull.*, No. 643, Bureau of Foreign and Domestic Commerce, U. S. Department of Commerce, Washington 1929.

"International Control of Minerals", *Am. Inst. Min. and Met. Eng.*, 129-150 (1925).

Appendix I

The Metals Reserve Company's terms of purchase of tungsten ores, originating in the different producing countries, are as follows:*

I. FOR ORES ORIGINATING IN THE UNITED STATES

In order further to stimulate domestic production of tungsten, and acting upon recommendation of the War Production Board, Metals Reserve Company has announced an extension until December 31, 1944, subject to the termination provisions hereinafter stated, of the period during which it will, upon the terms and conditions hereinafter stated, purchase domestic tungsten ores and concentrates at the base price of $30.00 per dry short ton unit of contained tungsten trioxide (WO_3).

"Qualified" producers of domestic tungsten may participate in this program upon the following terms and conditions:

1. "Qualified" Producers; Applications

A. *Definition.* A "qualified" producer is a domestic producer who in the year 1941 did not produce a quantity of tungsten materials having a recovered content of more than 13,500 units of WO_3, e.g. not more than 225 tons of 60 per cent WO_3 concentrates or the equivalent, and whose application as a "qualified" producer has been confirmed by Metals Reserve Company. Regardless of his prior total production heretofore from his other properties, any producer may apply for classification as a "qualified" producer with respect to any new property from which the foregoing quantity of tungsten materials was not produced in 1941.

B. *"Eligible" and "New" Producers.* Producers who have previously qualified as "eligible" or "new" producers under Metals Reserve Company's Tungsten Circulars dated May 8 or November 16, 1942, shall be deemed by Metals Reserve Company to be "qualified" producers; to have accepted the provisions of this Circular and thereby automatically amended their previously filed applications to conform to such provisions, and to have agreed to operate their respective properties at maximum possible capacity up to December, 1944, or the prior termination of this program, unless such producers shall have notified Metals Reserve Company,

---

* Because of the improvement of the tungsten supply situation in the United States, the Metals Reserve Co. on April 30, 1944 discontinued its premium price for domestic tungsten and on June 30, 1944 cancelled the foreign tungsten contracts except for a few long-term agreements.

prior to July 1, 1943, of their election to have their participation in the program governed by the terms and conditions of the Tungsten Circular dated November 16, 1942 and by the terms and conditions of their previously filed applications as an "eligible" or "new" producer, in which event the terms and conditions of said Circular and such applications shall remain applicable to such producers.

C. *Applications.* Producers who have not previously qualified as "eligible" or "new" producers under Metals Reserve Company's Circulars dated May 8 and November 16, 1942, must, in order to become "qualified" producers, properly fill in, in duplicate and mail to Metals Reserve Company, 811 Vermont Avenue, NW, Washington, D. C., "Application Form C—Qualified Producer" attached hereto, for confirmation by Metals Reserve Company.

2. Effective Period of Program: Termination Provision

The stipulated price will remain in effect until December 31, 1944, except that Metals Reserve Company may, on or after December 31, 1943, at any time give notice of its intention to terminate this program 30 days from the date of the giving of such notice. In the event of such termination, Metals Reserve Company will thereafter, at its option with respect to each "qualified" producer, either

A. Accept from such producer, f.o.b. same place and means of delivery theretofore used by such producer for sales to Metals Reserve Company, a quantity of material derived from such producer's mine or mines of the kind theretofore delivered by such producer, equal to such producer's "total unfilled production," and, upon and subject to the terms and conditions of this Circular, settle for such material at the base price of $30.00 per short ton unit, dry weight, of recoverable tungsten trioxide (WO_3) as defined herein; or

B. Settle in cash for such "qualified" producer's "total unfilled production" on the basis of $3.00 per short ton unit, dry weight, of recoverable tungsten trioxide (WO_3).

Such "total unfilled production" shall be an amount of material of the kind theretofore delivered by such producer, equivalent to such producer's average monthly production in short ton units, dry weight, of tungsten trioxide (WO_3) for the six calendar months preceding the effective date of termination of this program, multiplied by the number of months from such effective date to December 31, 1944, fractions pro rata.

3. High-Grade Concentrates

"Qualified" producers desiring to sell domestic high-grade concentrates to Metals Reserve Company or its authorized agents may do so upon the terms and conditions set forth below:

A. *Base Price.* $30.00 per short ton unit, dry weight, of contained tungsten trioxide (WO_3), f.o.b. railroad cars, Glen Cove, Long Island, New York, consigned to Metals Reserve Company care of the National Reconditioning Company, or f.o.b. railroad cars at such other point in the eastern United States, and consigned to such consignee, as Metals Reserve Company may designate.

B. *Specifications.* The aforesaid base price will apply without penalty only to concentrates meeting the following Standard Specifications:

Standard Specifications

		Scheelite	Hübnerite	Wolframite-Ferberite
Tungsten trioxide	(WO_3)	60.00%	60.00%	65.00%
Copper	(Cu)	0.05	0.03	0.03
Phosphorus	(P)	0.05	0.03	0.03
Arsenic	(As)	0.10	0.25	0.25
Bismuth	(Bi)	0.50	0.50	0.50
Molybdenum	(Mo)	0.40	0.40	0.40
Tin	(Sn)	0.10	1.50	1.50
Sulfur	(S)	0.50	0.50	0.50
Antimony	(Sb)	0.10	0.50	0.50
Manganese	(Mn)	1.00	—	—
Lead	(Pb)	0.10	0.10	0.10

C. *Penalties for Impurities.* Concentrates containing sufficient tungsten trioxide (WO_3) content to meet the above "Standard Specifications", but containing impurities in excess of "Standard Specifications", will be penalized as follows:

For each	0.01%	copper (Cu)	deduct 10¢ per short ton unit of WO_3
" "	0.01	phosphorus (P)	" " " " " " " "
" "	0.10	arsenic (As)	" " " " " " " "
" "	0.50	bismuth (Bi)	" " " " " " " "
" "	0.10	molybdenum (Mo)	" " " " " " " "
" "	0.10	tin (Sn)	" " " " " " " "
" "	0.10	sulphur (S)	" " " " " " " "
" "	0.10	antimony (Sb)	" " " " " " " "
" "	1.00	manganese (Mn)*	" " " " " " " "
" "	0.10	lead (Pb)	" " " " " " " "

D. *Quality.* Concentrates will not be accepted in lots of less than one (1) ton.

E. *Purchase Depots.* Concentrates of any grade will not be purchased by Metals Reserve Company at its Purchase Depots, except in Alaska.

4. Medium-Grade Concentrates

"Qualified" producers desiring to sell domestic medium-grade tungsten concentrates to Metals Reserve Company, *i.e.*, concentrates containing less tungsten trioxide (WO_3) than the above "Standard Specifications", down to and including 40 per cent tungsten trioxide (Wo_3), must negotiate

---

* Sheelite only.

special arrangements with Metals Reserve Company for the sale to it of such concentrates.

5. Low-Grade Mill Products

Metals Reserve Company has had erected at Salt Lake City, Utah, a chemical plant for the treatment of low-grade tungsten mill products not amenable to ordinary milling methods, thereby providing a market for such products. "Qualified" producers desiring to sell low-grade domestic tungsten mill products for treatment at this chemical plant may do so upon the terms and conditions set forth below, by applying to United States Vanadium Corporation, Agent for Metals Reserve Company, 568 West Eighth South Street, Salt Lake City, Utah.

A. *Mill Products Containing 15 per cent Tungsten Trioxide* (WO_3) *or Less.* Payment will be made for 90 per cent of the contained tungsten trioxide (WO_3) at the base price of $30.00 per short ton unit, dry weight, f.o.b. railroad cars, or trucks, designated siding or other delivery point at the plant site, less a treatment charge of $30.00 per short ton for material containing 3 per cent tungsten trioxide (WO_3), or less, plus 10¢ for each $\frac{1}{10}$ per cent of contained tungsten trioxide (WO_3) above 3 per cent fractions pro rata.

B. *Mill Products Containing in Excess of 15 per cent up to 40, Tungsten Trioxide* (WO_3). Payment will be made for 90 per cent of the contained tungsten trioxide (WO_3) up to and including 15 per cent, and for 100 per cent of the contained tungsten trioxide (WO_3) above 15 per cent up to 40 per cent, at the base price of $30.00 per short ton unit, dry weight, f.o.b. railroad cars, or trucks, designated siding or other delivery point at the plant site, less a treatment charge of $42.00 per short ton for material containing 15 per cent tungsten trioxide (WO_3) plus 10¢ for each $\frac{1}{10}$ per cent of contained tungsten trioxide above 15 per cent, fractions pro rata.

C. *Penalties for Impurities.* No penalties for impurities will be imposed.

D. *Quantity.* Mill products containing less than 5 per cent tungsten trioxide (WO_3) will be accepted in lots of 10 tons or more. Mill products containing in excess of 5 per cent tungsten trioxide (WO_3) will be accepted in lots of one ton or more.

6. Ores

A. **Salt Lake City.** Metals Reserve Company is now purchasing domestic crude tungsten ores f.o.b. Salt Lake City upon the terms and conditions stated below, for treatment at a custom mill. Mill sites and stockpile locations are under consideration, at which corresponding terms will apply. "Qualified" producers desiring to sell domestic crude tungsten ores that are amenable to treatment by standard milling methods and/or auxiliary chemical treatment for maximum tungsten recovery, may do so upon the terms and conditions set forth below, by applying to United States Vanadium Corporation, Agent for Metals Reserve Company, 568 West Eighth South Street, Salt Lake City, Utah.

(a) *Price.* Payment will be made for 85 per cent of contained tungsten trioxide (WO_3) at $30.00 per short ton unit, dry weight, f.o.b. railroad cars, or trucks, designated siding or other delivery point at the plant site, less $3.00 per short ton for milling and an additional charge of $2.00 per short ton unit, dry weight, of tungsten trioxide (WO_3) content to cover chemical treatment, fractions pro rata.

(b) *Penalties far Impurities.* No penalties for impurities will be imposed.

(c) *Quantity:* Ores containing 5 per cent tungsten trioxide (WO_3) or less will be accepted in lots of ten (10) tons or more. Ores containing in excess of 5 per cent tungsten trioxide (WO_3) will be accepted in lots of one (1) ton or more.

B. **Purchase Depots.** Metals Reserve Company will also purchase domestic crude tungsten ores on the above terms and conditions at Purchase Depots established by Metals Reserve Company (see list attached), except that a charge of $3.00 per short ton unit, dry weight, of tungsten trioxide (WO_3) up to a maximum charge of $9.00 per ton, fractions pro rata, will be made to cover freight and handling costs.

General Procedure

In the case of all purchases by Metals Reserve Company, the following general terms and conditions, in addition to those set forth above, will apply:

7. Weighing, Sampling and Analysis

A. Weighing, sampling and analysis will be at the expense of Metals Reserve Company.

B. Each shipment on arrival will be weighed, sampled and analyzed by the usual standard methods.

C. The weight of each shipment will be determined by a weighmaster on scales designated by Metals Reserve Company. A weight ticket will be furnished for each shipment.

D. Each shipment will be sampled and analyzed (this includes moisture determination) by an analyst designated by Metals Reserve Company.

E. All final samples will be divided into four pulps which will be sealed in the presence of the producer or his representative, if present, and will be distributed as follows:

(a) The producer or his representative will upon request receive one pulp.

(b) Metals Reserve Company or its representative will receive one pulp.

(c) The other two pulps will be filed for umpire.

F. The Metals Reserve Company pulp will be analyzed. The producer may, if he desires, and at his own expense, have his pulp analyzed and have results compared. Settlement may then be made by agreement. If agreement can not be reached one of the filed pulps may be sent to an umpire analyst, mutually acceptable to both parties. The results of the umpire analysis must be accepted by both parties and the umpire costs borne by the party having the greatest difference in analysis results.

8. Payment

Promptly after analysis is obtained, including moisture determination, settlement sheet together with check in payment will be mailed to producers.

9. Rejection

Metals Reserve Company, through its Agents, reserves the right to reject shipments where it is found that such materials are not suitable for treatment at the plants. Any and all material rejected must be removed by producer within 15 days after mailing of notice of rejection. Any and all material not removed as above provided may, at the option of Metals Reserve Company, or its Agents, be removed or otherwise disposed of by Metals Reserve Company, or its Agents, without any liability whatsoever therefor or in connection therewith.

If any "qualified" producer has any doubt as to the acceptability of his product, it is suggested that such producer submit a sample thereof to National Reconditioning Company, Glen Cove, Long Island, New York, in the case of material containing 40 per cent or more tungsten trioxide (WO_3), and to United States Vanadium Corporation, Agent for Metals Reserve Company, Salt Lake City, Utah, in the case of material containing less than 40 per cent tungsten trioxide (WO_3). For concentrates containing 40 per cent or more tungsten trioxide (WO_3) a 25-pound sample is adequate, but for very low-grade material, a 200-pound sample is needed. For intermediate-grade concentrates a sample of intermediate size should be provided.

10. Direct Shipments to Consumers of Concentrates Sold to Metals Reserve Company

If any "qualified" producer desires to sell concentrates to Metals Reserve Company upon the general terms and conditions of this Circular and to deliver such concentrates directly to the consumer, the necessary arrangements therefor should be made by such producer and the consumer, subject to the approval of Metals Reserve Company with respect to weighing, sampling, analysis and waiver of impurities and provided the consumer has obtained the necessary War Production Board allocations. In such cases the producer should promptly notify Metals Reserve Company the details of such arrangements and furnish full information as to the quantity and grade of the concentrates which are to be purchased by Metals Reserve Company and resold by it to the consumer. Upon receipt of such notice and information, Metals Reserve Company will issue to the producer instructions covering shipment and settlement.

11. Custom Mills and Dealers

Any custom mill or dealer who ships high or medium-grade concentrates entitled to the $30 base price set forth herein directly to consumers may make application to Metals Reserve Company for a standard contract for the sale of such concentrates to Metals Reserve Company at such base price, which contract will require such custom mill or dealer to pass back to the proper "qualified" producer or producers the full benefit of the increase in price announced by Metals Reserve Company in its Tungsten Circular of November 16, 1942.

II. For Ores Originating in China

(a) Price of Tungsten

The *base price* of the tungsten shall be determined by the *average* market price for "Chinese wolfram ore 65 per cent WO_3 c.i.f. New York", as quoted in the weekly issue of the "E. & MJ Metal and Mineral Markets" (of the "Engineering and Mining Journal" published by McGraw-Hill Publishing Company, Inc., New York, N. Y.) for the two-month period preceding the date on which the vessel carrying the tungsten arrives at the United States port of destination, less the United States customs duty if said quotation price includes such duty. The aforesaid base price shall be the purchase price for the tungsten less the penalties, if any, as hereinafter provided.

(b) Quality of Tungsten

(1) *Tungsten Specifications not Subject to Penalties.* The tungsten shall conform to the following specifications and requirements:

WO_3	Sixty-five per cent	(65.00%) min
Tin	One and fifty one-hundredths per cent	(1.50%) max
Arsenic	Twenty one-hundredths per cent	(0.20%) max
Copper	Twelve one-hundredths per cent	(0.12%) max
Phosphorus	Five one-hundredths per cent	(0.05%) max
Antimony	Five one-hundredths per cent	(0.05%) max
Bismuth	Forty one-hundredths per cent	(0.40%) max
Molybdenum	Forty one-hundredths per cent	(0.40%) max
Sulfur	One per cent	(1.00%) max

As to the copper, phosphorus and sulfur content, notwithstanding the aforesaid maximum specifications, the deliveries in each six (6) month period from the date hereof shall have a weighted average of not more than six one-hundredths per cent (.06 per cent) copper content, thirty-five one-thousandths per cent (.035 per cent) phosphorus content, and fifty one-hundredths per cent (.50 per cent) sulfur content.

(2) *Tungsten Penalties.* The following penalties with respect to the tungsten are hereby agreed to:

WO_3 Content

If the WO_3 content is under sixty-five per cent (65%) but is not below sixty per cent (60%), then there shall be deducted from the aforesaid base price for each per cent that the WO_3 content is under sixty-five per cent (65%) down to and including sixty per cent (60%), six cents ($0.06) per unit WO_3 per short ton of two thousand (2,000) pounds per ton net dry weight—fractions in proportion.

Tin Content

If the tin content exceeds one and fifty one-hundredths per cent (1.50%) but does not exceed two and twenty one-hundredths per cent (2.20%), then there shall be deducted from the aforesaid base price for each ten one-hundredths per cent (.10%) over one and fifty one-hundredths per cent (1.50%, four cents ($0.04) per unit WO_3 per short ton of two thousand (2,000) pounds per ton net dry weight—fractions in proportion.

Arsenic Content

If the arsenic content exceeds twenty one-hundredths per cent (.20%) but not fifty one-hundredths per cent (.50%), then there shall be deducted from the aforesaid base price the following:

If the arsenic content exceeds twenty one-hundredths per cent (.20%) up to and including twenty-five one-hundredths per cent (.25%)—six cents ($0.06) *or*	Per unit of WO_3 per short ton of two thousand (2,000) lbs. per ton net dry weight.
If the arsenic content exceeds twenty-five one-hundredths per cent (.25%) up to and including thirty one-hundredths per cent (.30%)—twelve cents ($0.12) *or*	
If the arsenic content exceeds thirty one-hundredths per cent (.30%) up to and including fifty one-hundredths per cent (.50%)—eighteen cents ($0.18).	

(3) *Tungsten Rejection Basis.* Tungsten not conforming to the following specifications will be rejected:

WO_3	Sixty per cent	(60.00%) min
Tin	Two and twenty one-hundredths per cent	(2.20%) max
Arsenic	Fifty one-hundredths per cent	(0.50%) max
Copper	Twelve one-hundredths per cent	(0.12%) max
Phosphorus	Five one-hundredths per cent	(0.05%) max
Antimony	Five one-hundredths per cent	(0.05%) max
Bismuth	Forty one-hundredths per cent	(0.40%) max
Molybdenum	Forty one-hundredths per cent	(0.40%) max
Sulfur	One per cent	(1.00%) max

If the impurities exceed the percentages as set forth above, the Buyer shall have the right, in its sole discretion, to accept the tungsten and in that event further penalties shall be agreed upon.

III. For Ores Originating in Bolivia

The ores and/or concentrates delivered shall meet the following specifications and requirements and shall be paid for according to the following schedule of prices:

Class A: High-Grade Wolfram Concentrates

Standard quality will be: WO_3 minimum 65 per cent; tin maximum 1.5 per cent; arsenic maximum 1.0 per cent; sulfur maximum 1.5 per cent; copper maximum 0.8 per cent, and will be paid for at $22.60 per short ton (2,000 lbs.) unit of WO_3 net dry weight, on an f.o.b. ocean steamer, South American port basis.

Penalties and Bonuses. In case of deviations from the above analysis, the following penalties or bonuses will be paid:

Penalties: For each per cent WO_3 below 65 per cent down to and including 60 per cent, a penalty of $0.045 per short ton unit of WO_3, net dry weight, fractions in proportion. For each further per cent WO_3 below 60 per cent down to and including 55 per cent, a penalty of $0.09 per short ton unit of WO_3, net dry weight, fractions in proportion. If the WO_3 content should be less than 55 per cent, Buyers have the option of rejecting the material under this Clause, or accepting it at a mutually agreed allowance.

Tin. If tin exceeds 1.6 per cent, a penalty of $0.03 per short ton unit of WO_3 for each 0.1 per cent tin above 1.5 per cent will be paid by the Seller.

Arsenic. If the arsenic content exceeds 1.0 per cent but is less than 1.5 per cent the Seller will pay a penalty of $0.15 per short ton unit of WO_3. If the arsenic content exceeds 1.5 per cent, but is less than 2.0 per cent, the Seller will pay a penalty of $0.20 per short ton unit of WO_3.

If the arsenic content is less than 3.0 per cent but more than 2.0 per cent, the Seller will pay a penalty of $1.00 per short ton unit of WO_3. The Buyer is not obligated to accept more than 10 tons per month of this last class of material having arsenic content between 2.0 per cent and 3.0 per cent.

Copper and Sulfur. Any ores and/or concentrates with content of copper above 0.8 per cent, or content of sulfur above 1.5 per cent but which is not subject to the rejection options set forth below, shall be paid for at $21.60 per short ton unit of WO_3 subject to the above mentioned penalties for WO_3, tin and arsenic.

Rejection Options. The Buyer has the option of rejecting under Class A, or of purchasing subject to the above mentioned penalties, all ores and/or concentrates with:

a) WO_3 content below 55 per cent; or
b) Arsenic content above 3.0 per cent; or
c) Copper content above 1.6 per cent; or
d) Sulfur content above 2.0 per cent

Bonuses. For ores and/or concentrates which, on account of their low impurities and high WO_3 contents, are better quality than standard Bolivian material, premiums will be paid on the following basis:

If the tin content is less than 1 per cent: arsenic less than 0.2 per cent; sulfur less than 0.75 per cent and WO_3 content not less than 65 per cent, the following prices will govern:

For 65% WO_3	$22.70	$US	per short ton unit
For 66% WO_3	$22.80	$US	" " " "
For 67% WO_3	$22.90	$US	" " " "
For 68% WO_3	$23.00	$US	" " " "
For 69% WO_3	$23.10	$US	" " " "
For 70% WO_3 and above	$23.20	$US	" " " "

Class B: Low-Grade Wolframite Concentrates

Concentrates or ores containing from 55 per cent WO_3 to 30 per cent WO_3 in the form of wolframite will be subject to the same penalties for WO_3 tin, arsenic, copper and sulfur, and to the same rejection options for impurities as for Class A ores and concentrates and will pay an additional penalty of $US 1 per short ton unit of WO_3 (complex ores of wolfram and tin covered by Class F are excepted). Buyer shall have option of rejecting ores or concentrates of this Class below 30 per cent WO_3.

Class C: High-Grade Scheelite Concentrates

Standard quality will be: WO_3 minimum 60 per cent; tin maximum 0.5 per cent; arsenic maximum 0.5 per cent; sulfur maximum 1.0 per cent; copper maximum 0.2 per cent; and will be paid for at $22.60 per short ton (2000 lbs.) unit of WO_3 net dry weight on an f.o.b. ocean steamer, South American port basis.

Penalties and Bonuses. In case of deviations from the above analysis the following penalties or bonuses will be paid:

Penalties. WO_3: For each per cent WO_3 below 60 per cent down to and including 55 per cent, a penalty of $0.09 per short ton unit of WO_3, net dry weight, fractions in proportion.

If the WO_3 content should be less than 55 per cent Buyers have the option of rejecting the material under this Clause or accepting it at a mutually agreed allowance.

Tin. If tin exceeds 0.5 per cent a penalty of $US 0.03 per short ton unit of WO_3 for each 0.1 per cent tin above 0.05 per cent will be paid by the Sellers.

Arsenic. If the arsenic content exceeds 0.5 per cent but is less than 1 per cent, the Sellers will pay a penalty of $US 0.15 per short ton unit of WO_3.

Copper and Sulfur. Any ores and/or concentrates with content of copper above 0.2 per cent or content of sulfur above 1.0 per cent, but which is not subject to the rejection options set forth below, shall be paid for at $21.60 per short ton unit of WO_3, subject to the above mentioned penalties for WO_3, tin and arsenic.

Rejection Options. The Buyer has the option of rejection under Class C or of purchasing subject to the above mentioned penalties, all ores and/or concentrates with:

(a) WO_3 content below 55 per cent; or
(b) Tin above 1 per cent; or
(c) Arsenic above 1 per cent; or
(d) Copper above 0.5 per cent; or
(e) Sulfur above 1.5 per cent

Bonuses. For ores and/or concentrates which, on account of their low impurities and high WO_3 contents are better quality than standard Bolivian material, premiums will be paid on the following basis: If tin content is less than 0.2 per cent, arsenic less than 0.1 per cent, sulfur less than 0.75 per cent, and WO_3 content not less than 60 per cent, the following prices will govern:

For 60% WO_3	$22.70	per short ton unit
" 61% "	$22.80	" " " "
" 62% "	$22.90	" " " "
" 63% "	$23.00	" " " "
" 64% "	$23.10	" " " "
" 65% " and above	$23.20	" " " "

Class D: Low-Grade Scheelite Concentrates and Ores

Concentrates or ores containing less than 55 per cent WO_3 and more than 30 per cent WO_3 will be subject to the same penalties as for WO_3—tin, arsenic, copper and sulfur, and to the same rejection options for impurities, as for Class C ores, and will pay an additional penalty of $US 1.00 per short ton unit of WO_3 (Complex ores of tungsten and tin specified in Class F are excepted).

Rejection Option. The Buyer has the option of rejecting under Class D or of purchasing subject to the above mentioned penalties, all ores and concentrates containing less than 30 per cent WO_3. The conditions stipulated in Class D do not apply to the special ores and concentrates covered by Classes E, F and G.

Class E

For the "Juliana" clean low-grade Scheelite concentrates which are of recognized high quality on account of their negligible tin, arsenic and sulfur contents, Buyer will purchase on the basis of $20.10 per short ton unit of WO_3, net dry weight, on an f.o.b. ocean steamer, South American port basis, as long as they meet the following specifications: WO_3 more than 30 per cent; sulfur less than 1 per cent; arsenic less than 0.05 per cent; tin less than 0.05 per cent.

Class F: Complex Tungsten-Tin Ores and Concentrates

Ores containing from 20 to 45 per cent WO_3 in the form of scheelite or mixed wolfram and scheelite and 18 to 35 per cent tin will be paid for at the rate of $US 19.10 per short ton unit of WO_3, net dry weight, on an f.o.b. ocean steamer, South American port basis. Buyer will also pay for 90 per cent of the tin content on the terms paid for Bolivian tin ores in accordance with the tin contract of November 4, 1940. Those exporters of this class of ore who prefer to make their own arrangements for refining their ores in the United States are free to do so, and Buyer will buy the tungsten concentrates so produced under the terms of this contract; provided, however, delivery shall be made to Buyer in New York without any obligation to make the 80 per cent advance payment.

Class G: Low-Grade Scheelite with Barium Sulfate Content

Buyer will purchase on a basis of $US 19.60 per unit of WO_3, net dry weight, on an f.o.b. ocean steamer, South American port basis, low-grade scheelite with content of barium sulfate from the Asuncion mine as long as the WO_3 content is not less than 30 per cent.

IV. FOR ORES ORIGINATING IN ARGENTINA

High-Grade Wolfram Concentrates

Standard quality will be: WO_3 minimum 65 per cent; tin maximum 1.5 per cent; arsenic maximum 1.0 per cent; sulfur maximum 1.5 per cent; copper maximum 0.8 per cent, and will be paid for at $21.00 per short ton (2,000 lbs) unit of WO_3 net dry weight, on a c.i.f. New York basis.

Penalties and bonuses as well as conditions governing classes A–F are the same as those for ores originating in Bolivia.

V. For Ores Originating in Mexico

1. **High-Grade Ores.** The base price per unit of contained tungsten trioxide (WO_3) delivered f.o.b. railroad cars at the plant of National Reconditioning Company, Glen Cove, Long Island, New York, U. S. A., or f.o.b. railroad cars at such other point in the New York area as Buyer may designate (with cost of freight and insurance from United States port of entry to Glen Cove, Long Island, New York, to be for Buyer's account and the Seller to be reimbursed for freight from United States port of entry if paid by Seller) shall be as set forth in the table below, all fractions in proportion, less penalties as hereinafter specified:

Base Price per Short Ton Unit

% WO_3	Scheelite Ores & Concentrates	Wolframite (Hübnerite-Ferberite Ores & Concentrates)
65 and over	$22.60	$22.60
64	22.60	22.55
63	22.60	22.51
62	22.60	22.46
61	22.60	22.42
60	22.60	22.37
59	22.51	22.28
58	22.42	22.19
57	22.33	22.10
56	22.24	22.01
55	22.15	21.92
54	21.06	20.83
53	20.97	20.74
52	20.88	20.65
51	20.79	20.56
50	20.70	20.47
49	20.61	20.38
48	20.52	20.29
47	20.43	20.20
46	20.34	20.11
45	20.25	20.02
44	20.16	19.93
43	20.07	19.84
42	19.98	19.75
41	19.89	19.66
40	19.80	19.57

Penalties

Scheelite Ores and Concentrates:

Arsenic:	over .5% but less than 1%	15¢	per short ton unit of WO_3.
	1% or over	30¢	
Sulfur:	over 1% but less than 1.5%	$1.00	
	1.5% or over	$1.25	
Copper:	over .2% but less than .5%	$1.00	
	.5% or over	$1.25	
Tin:	for each .1% tin above .5%	3¢	

Wolframite (Hübnerite-Ferberite) Ores and Concentrates:

Arsenic:	Over 1.0% but less than 1.5%	15¢	per short ton unit WO_3
	1.5% or over but less than 2.0%	20¢	
	2.0% or over but less than 3.0%	$1.00	
	3.0% or over	$1.15	
Sulfur:	over 1.5% but less than 2.0%	$1.00	
	2.0% or over	$1.25	
Copper:	over .8% but less than 1.6%	$1.00	
	1.6% or over	$1.25	
Tin:	for each .1% tin above 1.5%	3¢	

If a shipment consists of mixed scheelite and wolfram material, it will be classified under the scheelite schedule if its WO_3 content is predominantly scheelite, or under the wolfram schedule if its WO_3 content is predominantly of the wolfram type.

Buyer will make customs entry at port of entry and will attend to all phases of United States import duty. All other charges, including Mexican taxes and export duties, are for the account of and are to be paid by Seller.

2. **Low-Grade Ores.** The price per unit of contained tungsten trioxide (WO_3) delivered f.o.b. railroad cars at the Salt Lake City, Utah, U. S. A., Treatment Plant of Buyer, shall be as set forth in the table below, all fractions in proportion:

3% WO_3	$10.34 per unit
4% "	12.59 " "
5% "	13.94 " "
6% "	14.84 " "
7% "	15.48 " "
8% "	15.96 " "
9% "	16.34 " "
10% "	16.64 " "
11% "	16.89 " "
12% "	17.09 " "
13% "	17.26 " "
14% "	17.41 " "
15% "	17.54 " "

VI. For Ores Originating in Cuba

The base price per unit of contained tungsten trioxide (WO_3), delivered f.o.b. railroad cars at the plant of Wah Chang Trading Corporation, New York City, New York, or f.o.b. railroad cars at such other points in the New York City area as Buyer may designate, shall be as set forth in the table below, all fractions in proportion, less penalties as hereinafter specified:

% WO_3	Wolframite (Hübnerite-Ferberite)
65 and over	$21.00 per unit
64 “ “	20.95 “ “
63 “ “	20.91 “ “
62 “ “	20.86 “ “
61 “ “	20.82 “ “
60 “ “	20.77 “ “
59 “ “	20.68 “ “
58 “ “	20.59 “ “
57 “ “	20.50 “ “
56 “ “	20.41 “ “
55 “ “	20.32 “ “
54 “ “	19.23 “ “
53 “ “	19.14 “ “
52 “ “	19.05 “ “
51 “ “	18.96 “ “
50 “ “	18.87 “ “
49 “ “	18.78 “ “
48 “ “	18.69 “ “
47 “ “	18.60 “ “
46 “ “	18.51 “ “
45 “ “	18.42 “ “
44 “ “	18.33 “ “
43 “ “	18.24 “ “
42 “ “	18.15 “ “
41 “ “	18.06 “ “
40 “ “	17.97 “ “

Less *PENALTIES* as follows:

Tin:	$0.03 per short ton unit of WO_3 for each 0.1% in excess of 1.5%
Arsenic:	$0.15 per short ton unit of WO_3 if over 1.0% but less than 1.5%
	0.20 per short ton unit of WO_3 if 1.5% or over, but less than 2.0%
	1.00 per short ton unit of WO_3 if 2.0% or over, but less than 3.0%
	1.15 per short ton unit of WO_3 if 3.0% or over
Copper:	$1.00 per short ton unit of WO_3 if over 0.8% but less than 1.6%
	1.25 per short ton unit of WO_3 if 1.6% or over
Sulfur:	$1.00 per short ton unit of WO_3 if over 1.5% but less than 2.0%
	1.25 per short ton unit of WO_3 if 2.0% or over

VII. FOR ORES ORIGINATING IN PERU

The price per short ton unit of WO_3 is $22.60 f.o.b. steamer Peruvian Port, under terms and conditions of the Bolivian Tungsten Contract, except for penalties of $1.00 per unit of tungsten for sulfur content in excess of 2 per cent up to and including 3 per cent; $1.50 per unit of tungsten for sulfur content in excess of 3 per cent up to and including 4 per cent; and a penalty of $2.00 per unit of tungsten for sulfur content in excess of 4 per cent, fractions pro rata.

VIII. For Ores Originating in Brazil

The price per short ton unit of WO_3 is $21.00 Military Airport, Natal, Brazil or $22.60 f.o.b. steamer Santos or f.o.b. airplane Rio de Janeiro, Brazil. The terms and conditions are the same as those for Bolivian ores.

U. S. Commercial Company

Standard Schedule—Tungsten Concentrates

(This standard schedule shall become effective at 12:01 A.M. on April 10, 1945 and shall expire and be deemed withdrawn at midnight December 31, 1945)

	Prices for acceptable tungsten concentrates which are not subject to penalties and rejection limitations
% WO_3	Scheelite and Wolframite (Hübnerite and Ferberite)
65 and over	$13.00 per s.t.u. WO_3
64	12.80 “ “ “
63	12.60 “ “ “
62	12.40 “ “ “
61	12.20 “ “ “
60	12.00 “ “ “
59	11.90 “ “ “
58	11.80 “ “ “
57	11.70 “ “ “
56	11.60 “ “ “
55	11.50 “ “ “
54	11.40 “ “ “
53	11.30 “ “ “
52	11.20 “ “ “
51	11.10 “ “ “
50	11.00 “ “ “
49	10.90 “ “ “
48	10.80 “ “ “
47	10.70 “ “ “
46	10.60 “ “ “
45	10.50 “ “ “
44	10.40 “ “ “
43	10.30 “ “ “
42	10.20 “ “ “
41	10.10 “ “ “
40	10.00 “ “ “
39	9.90 “ “ “
38	9.80 “ “ “
37	9.70 “ “ “
36	9.60 “ “ “
35	9.50 “ “ “
34	9.40 “ “ “
33	9.30 “ “ “
32	9.20 “ “ “
31	9.10 “ “ “
30	9.00 “ “ “
Below 30	Reject

Standard Specifications

Wolfram (Hübnerite -Ferberite) (%)				Scheelite	
65.00	Min.	Tungsten Trioxide	(WO_3)	65.00%	Min.
0.05	Max.	Copper	(Cu)	0.05%	Max.
0.05	"	Phosphorus	(P)	0.05%	"
0.25	"	Arsenic	(As)	0.10%	"
1.00	"	Bismuth	(Bi)	0.25%	"
0.40	"	Molybdenum	(Mo)	0.40%	"
1.50	"	Tin	(Sn)	0.10%	"
0.50	"	Sulfur	(S)	0.75%	"
0.10	"	Antimony	(Sb)	0.10%	"
—		Manganese	(Mn)	1.00%	"

Penalties: All concentrates containing more than the maximum allowable percentage of any impurity will be assessed to basic charge of $20.00 per short ton of concentrates. In addition to this basic charge, the following penalties will be imposed.

Deduct 10¢ per s.t.u. WO_3:

For	each	0.02%	of	Copper (Cu)	above	standard specifications
"	"	0.01%	"	Phosphorus (P)	"	"
"	"	0.20%	"	Arsenic (As)	"	"
"	"	0.25%	"	Bismuth (Bi)	"	"
"	"	0.10%	"	Molybdenum (Mo)	"	"
"	"	0.20%	"	Tin (Sn)	"	"
"	"	0.20%	"	Sulfur (S)	"	"
"	"	0.10%	"	Antimony (Sb)	"	"
"	"	1.00%	"	Manganese (Mn)*	"	"

Fines

Fines (less than 200 mesh size) should be shipped separately and will be accepted subject to an additional penalty of $25.00 per short ton of concentrates. All coarse concentrate shipments (except coarse scheelite concentrates) which contain more than twenty per cent (20%) fines less than 200 mesh size, and all coarse scheelite concentrate shipments which contain more than sixty per cent (60%) less than 200 mesh size, will be accepted subject to an additional penalty of $50.00 per short ton of concentrates.

All other penalties will apply.

Tungsten-Tin Concentrates

Mixed tungsten-tin concentrates will be accepted only providing they contain at least 18 per cent Sn and at least 20 per cent WO_3. The tungsten will be paid for at the flat price of $9.00 per short ton unit of WO_3, less only a penalty for CaO Content of: $0.05 per s.t.u. WO_3 for each .10 per cent CaO in excess of .20 per cent.

Payment will be made for 90 per cent of the tin content on the terms and prices (including deductions for smelting and impurities) being paid gener-

---

* Applies to scheelite only.

ally by U. S. Commercial Company from time to time for Bolivian tin concentrates.

No roasting tungsten-tin concentrates will be accepted.

Shipping

Shipments shall be made in lots of between 25 and 30 long tons net, except as otherwise provided in the contract proper.

Terms and Definitions

All prices are for delivery f.o.b. ocean vessel at foreign port of ports, or f.o.b. railroad cars U. S. border port or ports of entry, hereinbefore described in the contract proper and pursuant to the terms thereof. All prices, charges, penalties, deductions, and quantities are on a "fractions pro rata" basis.

"s.t.u." equals short ton unit (20 lbs. avoirdupois) dry weight.
"short ton" equals 2,000 lbs. avoirdupois dry weight.
"long ton" equals 2,240 lbs. avoirdupois.

This Standard Schedule shall become effective at 12:01 A.M. on April 10, 1945 and shall expire and be deemed withdrawn at midnight December 31, 1945.

All deliveries of concentrates made during the effective term of this schedule shall be at the prices and upon the terms of this schedule.

All prices and penalties are expressed in terms of United States Currency.

Appendix II

Chinese Wolfram ore has been sold in Europe under the so-called Hamburg Contract "A", as follows:

The price is reckoned per unit of WO_3 of 2240 lbs. (1016 kilos) net dry weight, cif European ports.

The ore must be of good merchantable quality, containing min. 65 per cent WO_3, max. 1.5 per cent Sn, max. 0.2 per cent As. In case of deviation regarding quality and/or contents buyers have not right to reject the goods, provided the WO_3 contents are not under 55 per cent and/or the As contents are not over 2 per cent, but they have to take delivery with the following allowances to be granted by sellers.

WO_3 Contents: In case the WO_3 content should be under 65% the following allowances are to be made:

For each percent WO_3 under 65% down to and including 60%:	3d.	per unit WO_3 per ton of 1016 kilos net dry weight—fractions in proportion.
For each further percent WO_3 under 60% down to and including 55%:	6d.	

If the WO_3 contents should be less than 55% buyers have the option of rejecting the goods or of accepting same at an allowance mutually agreed upon or (failing agreement) fixed by arbitration, such option to be declared by buyers within 8 days after receipt of assay certificate.

Sn Contents: If the Sn Contents exceed 1.5% but do not exceed 1.6% buyers have to accept the goods as good delivery. Should the Sn Contents exceed 1.6% sellers have to allow to buyers for each one tenth percent over 1.5% 2d. per unit WO_3 per ton of 1016 kilos net dry weight—fractions in proportion.

As Contents: Sellers have to grant to buyers the following allowances:

If the full As contents exceed 0.2% up to and including 0.25%:	3d.	per unit WO_3 per ton of 1016 kilos net dry weight.
If the full As contents exceed 0.25% up to and including 0.30%:	6d.	
If the full As contents exceed 0.30% up to and including 0.70%:	9d.	

For each further ½ per cent or part thereof over 0.70 per cent an additional 3d. per unit WO_3 per ton of 1016 kilos, net dry weight.

If the assay exceeds 0.2 per cent As a second assay is to be made by another laboratory mutually agreed upon by the two parties, the mean of the two results being final. The cost of the second assay is also to be equally divided between buyers and sellers.

If the As Contents exceed 2 per cent buyers have the option of rejecting the goods or of accepting same at an allowance mutually agreed upon or (failing agreement) fixed by arbitration, such option to be declared by buyers within 8 days after receipt of the assay certificate.

Buyers have the right to deduct the before mentioned allowances from the payment of final invoice.

The Hamburg Contract "B", intended for transaction of ores other than those originating from China is exactly the same as the Hamburg Contract "A", with the exception of the wording of the Force Majeure clause.

Appendix III

Post-War Tungsten Situation

The special characteristics of tungsten for heat resistance and acid proofing has made tungsten a very important metal, both in time of war and in time of peace. During the last quarter of a century, no other metal in such comparatively small quantity has made so profound an influence upon the conduct and development of industries as has tungsten. In spite of the discovery of its various new uses during recent years, the future of tungsten is still pregnant with great possibilities. It is well that the producers of tungsten should bear this in mind in looking forward to its future applications in the post-war era.

During World War II, the Germans were the first to use tungsten carbide core in high velocity armour piercing projectiles. It was these tungsten projectiles, more than Rommel that almost made German's North African campaign a success. The famous British tanks virtually "melted" when hit by these tungsten carbide projectiles. Two years later the United States Army perfected similar anti-tank projectiles which were used to stop Von Rundstedt's Belgian Bulge. The German Tiger and Panther tanks were no longer effective when they were answered by the American carbide armour piercing projectiles. The core of the projectiles is virtually unmarked after passing through the armour plate of the tanks. After penetration the core breaks up into lethal pieces, scattering in all directions inside the tank, often setting fire to the tank.

For a time, America had a program of producing such projectiles that required a supply of at least thirty million pounds of tungsten metal or about 38,000 tons of ore with 60 per cent WO_3.

Tungsten is still the hardest metal yet made use of by man. Its application for gas turbine, jet propulsion or any high-heat resistance is unlimited. Its quality cannot be equalled or substituted by molybdenum or any other metal.

With the cessation of war it is up to the producers of tungsten to find outlets for its use in peacetime industry to replace the gap left open by termination of its wartime uses. This can be realized if the producers of tungsten have the necessary foresight and vision.

Because of the war the world production of tungsten has undoubtedly increased. Many countries which have scarcely produced any appreciable amount of tungsten before World War II such as Brazil, Peru, Belgian Congo, Union of South Africa, Rhodesia, and other South African countries, have now become important producers. New mines have been uncovered in old producing countries such as the United States, Bolivia, Argentina and Australia. The production in China, Burma, Siam and Indo-China, has not been increased during World War II because of lack of transportation to the Western World and the "scorched earth" policy of China towards Japan.

The total world production in 1945 has been estimated at about 38,000 tons. The trend is towards an increase in the production of the Far East and a decrease in the production of North and South America. The production of about 38,000 tons in the year 1945 in which the market ranged about twenty four dollars per short ton unit will probably be maintained for some time.

The mining of tungsten is no different from the mining of other minerals. A producer is reluctant to close his mine voluntarily. He hopes either for the discovery of a large deposit that will reduce his cost and so make operation profitable or for the rise in the market or the closing down of mines. This is what happened after World War I and history may repeat itself if no constructive program is forthcoming.

We do not believe that an international cartel arrangement to control production and prices is practical because if nothing else it is against the the law of the U. S. A. whose consumption is by far the largest in the world. Nor do we believe that any increase in the U. S. import tariff will help American producers even if the Congress is prevailed upon to act. In short, any program that is contrary to the natural law of supply and demand will in the long run fail as it has failed in many countries for many commodities.

The only constructive program that has the seeds of enduring success is to increase the demand to meet the supply. Many new uses have been found in a small way for tungsten and these can be developed to meet the production. To advance this procedure, the suggestion has been made that an International Tungsten Producers Research Association be organized whose primary purpose would be to promote research in the development of new uses, develop new applications of old uses and in general to extend the scope of tungsten products in the world of industry.

The characteristics of molybdenum as a metal are to a great extent similar to that of tungsten. Yet the world consumption of molybdenum has increased more than thirtyfold during the past twenty years while in the same period the consumption of tungsten has increased less than five-fold. The reason is that a member of the molybdenum industry which has consistently produced more than 90 per cent of the world production of molybdenum has with foresight carried on research to develop new uses for molybdenum.

Tungsten has always been a stepchild in the world market because it is produced by so many companies in so very many countries. For this reason any program such as is envisaged by the International Tungsten Producers Research Association must have as its objective the finding of new uses rather than the curtailment of production for the stabilization of "world market prices." The Association's objective should be constructive by creating new demands rather than by the old fashioned method of controlling supply. While this approach may be slow in achieving results, it will be constructive and in the end enduring.

Funds for the establishment of such an association may be apportioned by the leading producers of China, United States, Burma, Bolivia, Brazil, Peru, Argentina, Siam, Indo-China, Belgian Congo, Union of South Africa, Rhodesia, Portugal and Spain. Figuring the production of the post World War to be the same as that of 1945 which was certainly not a high priced market for tungsten, there will be a total production of 2,280,000 units. A membership contribution of 25 cents per unit of production by large producers to the Research Association is only a trifle and a great investment on the part of these producers who already have huge outlays in their mines. If only 75 per cent of the world producers join, there will be an annual income of $428,000 which under favorable American conditions can be productive of tremendous benefit.

It is important that the funds come from the producers and not from the governments whose participation may defeat the very purpose of the Association. As the Association will not be profit-making, contributions will be tax exempt.

Research laboratories should be established in the United States because of the facilities and the personnel there and cooperation with universities and research institutes promoted. Any discovery made by the Association should be public property and the results of all research should be published for the benefit of members.

Appendix IV

References Relating to Tungsten Alloys*

Al-W

F. Wohler and F. R. Michel, *Liebig's Ann.* **115**, 102 (1860).

L. Gillet, *Compt. rend.* **132**, 1112 (1901); also *Bull. Soc. d'Encour* **101** (ii), 228 (1902) and *Genie Civil*, **41**, 396 (1902).

W. Campbell and J. A. Mathews, *J. Am. Soc.* **24**, 256 (1902).

H. Schirmeister, *Stahl Eisen*, **35**, 998 (1915).

W. D. Clark, *J. Inst. Metals*, **66**, 271 (1940).

---

* Mainly taken from "Constitution of Alloys Bibliography," by J. L. Haughton. Monograph and Report Series, No. 2, The Institute of Metals, London, 1942.

As-W E. Heinerth and W. Biltz, *Z. anorg. Chem.* **198,** 169 (1931).

Au-W Bernoulli, *Pogg. Annalen,* **111,** 573 (1860).

B-W A. Binet du Jassonneiz, *Compt. rend.* **141,** 191 (1905) and *Bull. Soc. Chim. France* (iii) **35,** 278 (1906).
F. Haile and W. Thury, *Z. anorg. Chem.* **249,** 229 (1942).

Bi-W Ch. L. Sargent, *J. Am. Soc.* **22,** 784 (1900).

C-W W. Hempel, *Z. angew. Chem.* **17,** 296, 321 (1904).
O. Ruff and R. Wunch, *Z. anorg. Chem.* **85,** 292 (1914).
M. R. Andrews, *J. Physical Chem.* **27,** 270, (1923).
E. Friedrich and L. Sittig, *Z. anorg. Chem.* **144,** 184 (1925).
K. Becker and F. Ebert, *Z. Physik.* **31,** 268 (1925).
M. R. Andrews and S. Dushman, *J. Physical Chem.* **29,** 462 (1925).
A. Westgren and G. Phragmen, *Z. anorg. Chem.* **156,** 27 (1926).
F. Skaupy, *Z. Elektrochem.* **33,** 487, (1927).
K. Becker and R. Holbling, *Z. angew. Chem.* **40,** 512 (1927).
K. Becker, *Z. Physik.* **51,** 418 (1928).
K. Becker, *Z. Metallkunde* **20,** 437 (1928).
K. Becker, *Z. Elektrochem* **34,** 640 (1928).
J. L. Gregg and C. W. Kuttner, *Trans. Amer. Inst. Min. Met. Eng.,* Inst. Metals Div. 581 (1929).
B. T. Barnes, *J. Physical Chem.* **33,** 688 (1929).
W. P. Sykes, *Trans. Amer. Soc. Steel Treat.* **18,** 968 (1930).
A. A. Ravdel, *Zhur. Russ. Fiziko Khimich. Obshch.* (Fiziki) **62,** 515 (1930).
C. Agte and H. Alterthum, *Z. Techn. Physik.* **11,** 182 (1930).
S. Takeda, "Anniversary Volume Dedicated to K. Honda" (Tohoku Imp. Univ.) 864, (1936).
U. Krawczynski, Dissertation Techn. Hochschule, Breslau (1936).

Co-W Haynes, *J. Ind. Eng. Chem.* **5,** 189 (1913).
D. Kremer, *Abhandl. Inst. Metalhutt. u. Elektromet. K. Techn. Hochschule Aschen,* (1916), **1,** (2), 13.
K. Kreitz, *Metall. u. Erz.* **19,** 137 (1922).
W. Geiss and J. A. M. van Liempt, *Z. Metallkunde* **19,** 113 (1927).
W. Koster and W. Tonn, *Z. Metallkunde* **24,** 296 (1932).
C. Agte, K. Becker and Frhr. v. Goler, *Metallwirtschschaft* **11,** 447 (1932); and *Techn.-wiss. Abhandl. Osram-Konzern* **3,** 12 (1934).
W. P. Sykes, *Trans. Amer. Soc. Steel Treat.* **21,** 385 (1933).
S. Takeda, "Anniversary Volume Dedicated to K. Honda" (Tohoku Imp. Univ.) 864, (1936).
A. Magneli and A. Westgren, *Z. anorg. Chem.* **238,** 268 (1938).
M. M. Babich, E. N. Kislyakova and J. S. Umanskiy, *Zhur. Teknich. Fiziki* **8,** 119 (1938), and *Tech. Physics U. S. S. R.* **5,** 189 (1938).
M. M. Babich, E. N. Kislyakova and J. S. Umanskiy, *Zhur. Teknich, Fiziki* **9,** 533 (1939) and *J. Physics* (U. S. S. R.) **1,** 309, (1939).

Cr-W

Haynes, *J. Ind. Eng. Chem.* **5,** 189 (1913).
M. N. Rich, U. S. Patent 1,731,267 (1927).
W. Koster, *Z. Metallk.* **25,** 26 (1933).
S. Isida, H. Assada and S. Higasimura, *Tokyo Teikoku-Daigaku Koku Kenkyuzyo Hokoku* **13,** 195 (1938); and *Tetsu to Hagane* **25,** 106 (1939).
C. L. Sargent, *J. Amer. Chem. Soc.*, **22,** 783 (1900).

Cu-W

F. A. Bernoulli, *Pogg. Ann.* **111,** 573 (1860); *Chem. News* **5,** 116 (1862).
C. L. Sargent, *Journ. Amer. Chem. Soc.* **22,** 783 (1900).
E. W. Von Siemens and J. G. Halske, German Patent 201283 (1906), 419388 (1921).
O. Rumschottel, *Metal u. Erz* **12,** 45 (1915) and *Abhandl. Inst. Metallhutt. u. Elektromet. K. Techn. Hochschule Aachen* **1** (1) 19, (1915).

Fe-W

Bernoulli, Loc. cit.
Schneider, *Oesterr, Zeitsch. Berg. und Huttenwesen* **33,** 257 (1885).
Osmond, *Compt. rend.* **104,** 985 (1887); **110,** 242, 346, (1890).
Koort, *Dingl. poly. J.* **270,** 166, 211 (1888).
Garrison, *J. Frank Inst.* **131,** 434 (1891); **132,** 54, 111 (1891); *Mon. scient.* (4) 6, 43, 274 (1892).
Wahl, *J. Frank. Inst.* **134,** 470 (1892).
Poleck and Grutzner, *Ber.* **26,** 35 (1893).
Behrens and Lingen, *Verh. K. Akad. Wetensch. Amsterdam* **2,** 151 (1893–94).
Benneville, *J. Amer. Chem. Soc.* **16,** 735 (1894).
Merle, *Mon. scient.* (4) **9,** 35 (1895).
Norton, *J. Amer. Chem. Soc.* **19,** 110 (1897).
Carnot and Goutal, *Compt. rend.* **125,** 148, 213 (1897); **128,** 207 (1899); *Ann. des Mines,* (9) **18,** 263 (1900); *Contributions a l'etudes des alliages*, Paris 493 (1901).
Le Chatelier, *Contributions a l'etude des Alliages* 413 (1901).
Mathews, *Elec. World and Engineer* **40,** 531 (1902).
Barrett, *Proc. Roy. Soc.* **69,** 480 (1902).
Guillet, *Compt. rend.* **139,** 519 (1904).
Harkort, *Metallurgie* **4,** 617, 639, 673 (1907).
D. Kremer, *Abhandl. Inst. Metallhutt u. Elektromet K. Techn. Hochschule, Aachen* **1** (2) 14, (1916).
K. Honda and T. Murakami, *Sci. Rep. Tohoku Imp. Univ.* (i) **6,** 264 (1918).
Daeves, *Zeitsch. anorg. Chem.* **118,** 67 (1921).
S. Ozawa, *Sci. Rep. Tohoku Imp. Univ.* (i) **11,** 333 (1922).
W. P. Sykes, *Trans. Amer. Inst. Min. Met. Eng.* **73,** 968, (1926).
H. Arnfelt, *Carnegie Schol. Mem. Iron Steel Inst.* **17,** 1, (1928).
S. Takeda, *Kinzoku no Kenkyu* 6,298 (1928); and *Tech. Rep. Tohoku Imp. Univ.* **9,** 101 (1930).
Z. Nishiyama, *Sci. Rep. Tohoku Imp. Univ.* (i) **18,** 359 (1929).
E. P. Chartkoff and W. P. Sykes, *Trans. Amer. Inst. Min. Met. Eng.*, Inst. Metals Div. 566 (1930).

W. P. Sykes, *Trans. Amer. Inst. Min. Met. Eng.*, Iron Steel Div. 307 (1931).

A. Osawa and S. Takeda, *Kinzoku no Kenkyu* **8,** 181 (1931).

W. P. Sykes and K. R. Van Horn, *Trans. Amer. Inst. Min. Met. Eng.* **105,** 198 (1933).

O. Landgraf, *Forschungsarb, Metallkunde u. Rontgenmetallographie* (12), 1934.

W. Jellinghaus, *Z. Anorg. Chem* **223,** 362 (1935).

H. Arnfelt and A. Westgren, *Jernkontorets Ann.* **119,** 185 (1935).

A. Westrgen, "Anniversary Volume Dedicated to K. Honda" (Tohoku Imp. Univ.) 852, (1936).

W. P. Sykes, *Trans. Amer. Soc. Metals* **24,** 541 (1936).

W. P. Sykes, *Trans. Amer. Soc. Metals* **25,** 953 (1937).

C. S. Smith, *J. Applied Physics* **12,** 817 (1941).

Hf-W

J. A. M. Van Liempt, *Nature* **115,** 194 (1925).

Hg-W

Feree, *Bl. Soc. Chim.* (3) **19,** 213 (1898).

J. L. Beckert, French Patent 539,234 (1921).

A. S. Russell and S. W. Rowell, *J. Chem. Soc.* 1884 (1936).

G. Tammann and J. Hinnuber, *Z. anorg. Ch.* **160,** 260 (1927).

G. Tammann and J. Hinnuber, *Zeit. anorg. Chem.* **160,** 249 (1927).

K. S. Jackson, A. S. Russell and J. Merrill, *J. Chem. Soc.* 2394 (1928).

N. M. Irvin and A. S. Russell, *J. Chem. Soc.* 891 (1932).

Mn-W

Arrivant, *Compt. rend.* **143,** 594 (1906).

Mo-W

P. Schwarzkopf and S. Burgstaller, French Patent 448,229 (1912).

F. G. Keyes, U. S. Patent 1,308,907 (1915); U. S. Patent 1,377,982 (1915).

Z. Jeffries, *Bl. Min. Eng.* 1230 (1916).

F. A. Fahrenwald, *Bl. Min. Eng.* **126,** 145 (1916).

F. A. Fahrenwald, *Bl. Min. Eng.* 1054 (1916).

F. A. Fahrenwald, U. S. Patent 1,236,384 (1916).

Z. Jeffries, *Trans. Amer. Inst. Min. Eng.* **56,** 600 (1917).

F. A. Fahrenwald, *Trans. Amer. Inst. Min. Eng.* **56,** 612 (1917).

Tammannschen Theorie, *Z. Anorg. Ch.* **107,** 1 (1919).

W. Geiss and J. A. M. van Liempt, *Z. anorg. Ch.* **128,** 355 (1923).

A. E. van Arkel, *Physics* **4,** 33 (1924).

W. Geiss and J. A. M. van Liempt, *Z. Metallk.* **16,** 317 (1924).

A. E. van Arkel. *Physics* **6,** 64 (1926).

A. E. van Arkel and C. Zwikker, *Z. ang. Ch.* **41,** 847 (1928).

Ni-W

Bernoulli, *Pogg. Annalen* **111,** 573 (1860).

Trowbridge and Sheldon, *Amer. J. Sci.* (3) **38,** 462 (1889); *Chem. News* **60,** 312, (1889).

Sargent, *J. Amer. Chem. Soc.* **22,** 783 (1900).

R. Irmann, *Abhandl. Inst. Metallhutt u. Elektromet. K. Techn. Hochschule Aachen* **1** (1) 27 (1915) and *Metall u. Erz.* **12,** 358 (1915).

Vogel, *Zeitsch. anorg. Chem.* **116,** 231 (1921).

K. Becker and F. Ebert, *Z. Physik.* **16,** 165 (1923).
K. Winkler and R. Vogel, *Arch. Eisenhuttenwesen* **6,** 165 (1932).
S. Takeda, "Anniversary Volume Dedicated to K. Honda" (Tohoku Imp. Unit.) 872 (1936).
F. K. Garyanov and V. I. Tretyakov, *Zhur. Tekhnich Fiziki* **8,** 1326 (1938).
F. H. Ellinger and W. P. Sykes, *Trans. Amer. Soc. Metals* **28,** 615 (1904).

Pb-W
S. Inouye, *Mem. Sci. Kyoto Univ.* **4,** 43 (1919/1921).

Pt-W
D. Kremmer, *Abhandl. Inst. Metallhutt. Elektromet. K. Techn. Hochschule Aachen,* **1,** (2) 18, (1916).
L. Muller, *Ann. Physik.* (v) **7,** 9 (1930).
R. Hultgren and R. I. Jaffee, *J. Applied Physics* **12,** 501 (1941).

Si-W
R. Frilley, *Rev. Met.* **8,** 502 (1911).

Sn-W
R. B. Wheatley, U. S. Patent 766,085 (1904); German Patent 131,514 (1901). German Patent 187,416 (1903).
Hannoversche Industriegesellschaft, German Patent 184,476 (1905).
J. G. Escard, *Genie Civil* **55,** 74, 85 (1909).
E. F. Northrup, *Bl. Min. Eng.* 1443 (1919).

Ta-W
W. v. Bolton, *Z. Elektroch.* **11,** 51 (1905).
J. W. Marden, U. S. Patent 1,731,255 (1924).
Siemens and Halske, Akt.-Ges.—German Patent 518,499 (1926).
C. Agte, K. Becker, *Z. Tech. Phys.* **11,** 108 (1930); *Phys. Z.* **32,** 67 (1931).

Th-W
L. v. Grotthuss-Call, *Met. Erz.* **10,** 844 (1913).
H. v. Wartenberg, J. Broy, R. Reinicke, *Z. Elektroch.* **29,** 214 (1923).
H. v. Wartenberg, J. Broy, R. Reinicke, *Z. Elektroch.* **29,** 217 (1923).
H. S. Cooper, U. S. Patent 1,732,326 (1925).
Siemens and Halske, Akt.-Ges.—German Patent 518,499 (1926).
W. Giess and J. A. M. Van Liempt, *Z. anorg. Ch.* **168,** 110 (1928).

Ti-W
W. Huppertz, *Met.* **1,** 416 (1904).

Zn-W
A. F. Bernoulli, *Pogg. Ann.* **111,** 580 (1860).

Zr-W
H. S. Cooper, *Trans. Am. electrochem. Soc.* **43,** 225 (1923).
Compagnie Des Lampes, French Patent 602,627 (1925).
J. H. De Boer and J. D. Fast, *Z. anorg. Ch.* **153,** 6 (1926).
A. Classen and W. G. Burgers, *Z. Krist.* **86,** 100 (1933).

Al-Cr-W
F. Weibke and U. Frhr. v. Quadt., *Z. Elektrochem.* **46,** 635 (1940).

Al-Cu-W
R. L. Roman, British Patent 19,543 (1893).
R. Wallace, U. S. Patent 567,757 (1896).
W. R. Whitmore and F. T. Sisco, *Journ. Ind. Chem.* **17,** 15 (1925).

Al-Sb-W
D. A. Roche, *Monit. Scient.* (4) **7,** 270 (1893).
D. A. Roche, *Monit. Scient.* (4) **7,** 269 (1893).

Al-Si-W
W. Manchot and A. Kieser, *Lieb. Ann.* **337,** 360 (1904).

C-Co-W
L. L. Wyman and F. C. Kelley, *Trans. Amer. Inst. Min. Met. Eng.*, Inst. Metals Div., 208 (1931).
W. P. Sykes, *Trans. Amer Inst. Min. Met. Eng.*, Inst. Metals Div. 227 (1931).
V. Adelskold, A. Sundelin and A. Westgren, *Z. anorg. Chem.* **212,** 406 (1933).
A. M. Korolkov and A. M. Lavler, *Metallurg.* (2) 53 (1934).
S. Takeda, "Anniversary Volume Dedicated to K. Honda" (Tohoku Univ. 864 (1936).
W. P. Sykes, *Trans. Amer. Inst. Min. Met. Eng.* **128,** 76 (1938).

C-Cr-W
V. Adelskold, A. Sundelin and A. Westgren, *Z. anorg Chem.* **212,** 404 (1933).
L. P. Mol'kov and I. V. Vikker, *Vestn. Metalloprom.* **16** (6) 75 (1936).

C-Fe-W
J. O. Arnold and A. A. Read, *Proc. Inst. Mech. Eng.* 223 (1914).
A. Hultgren, A. Metallographic Study of Tungsten Steels—New York and London (1920).
K. Daeves, *Z. anorg. Chem.* **118,** 67 (1921).
S. Ozawa, *Sci. Rep. Tohoku Imp. Univ.* (i) **11,** 333 (1922).
P. Oberhoffer, K. Daeves and K. Rapatz, *Stahl u. Eisen* **44,** 432 (1924).
A. Westgren and G. Phragmen, *Jernkontorets Ann.* **110,** 535 (1927) and *Trans. Amer. Soc. Steel Treat.* **13,** 539 (1928).
W. Zieler, *Arch. Eisenhuttenwesen* **3,** 61 (1929).
S. Takeda, *Kinzoku no Kenkyu* **6,** 455 (1929); *Tech. Rep. Tohoku Imp. Univ.* **9,** 483 (1930).
S. Takeda, *Kinzoku no Kenkyu* **6,** 509 (1929); also *Tech. Rep. Tohoku Imp. Univ.* **9,** 627 (1930).
W. A. Wood, *Phil Mag.*, (vii) **10,** 659 (1930).
S. Takeda, *Kinzoku no. Kenkyu* **7,** 409 (1930); also *Tech. Rep. Tohoku Imp. Univ.* **10,** 42 (1931).
A. Osawa and S. Takeda, *Kinzoku no Kenkyu* **8,** 181 (1931).
A. Westgren, *Jernkontorets Ann.* **116,** 1 (1933).
F. R. Morral, G. Phragmen and A. Westgren, *Nature* **132,** 61 (1933).

C-Ni-W
V. Adelskold, A. Sundelin and A. Westgren, *Z. anorg. Chem.* **212,** 407 (1933).
N. M. Zarubin and L. P. Mol'kov, *Vestn. Meatlloprom.* **15** (7) 93 (1935).
S. Takeda, "Anniversary Volume Dedicated to K. Honda" (Tohoku Imp. Univ.) 864 (1936).

C-Ta-W
C. Agte and H. Alterthum, *Z. Techn. Physik.* **11,** 182 (1930).

C-Ti-W
L. P. Mol'kov and I. V. Vikker, *Vestn. Metalloprom.* **16** (6) 75 (1936).

C-V-W	L. P. Mol'kov and I. V. Vikker, *Vestn. Metalloprom.* **16** (6) 75 (1936).
C-W-Zr	C. Agte and H. Alterthum, *Z. Techn. Physik.* **11,** 182 (1930).
Co-Cr-W	W. Koster, *Z. Metallkunde* **25,** 22 (1933).
Co-Fe-W	W. Koster and W. Tonn, *Arch. Eisenhuttenwesen* **5,** 431 (1932). B. A. Rogers, *Metals and Alloys* **4,** 69 (1933). W. P. Sykes, *Trans. Amer. Soc. Metals* **25,** 953 (1937). H. Cornelius, E. Osswald and F. Bollenrath, *Metallwirtschaft* **16,** 393 (1937).
Cr-Fe-W	C. Agte, *Forschungen u. Fortschritte* **9,** 42 (1933).
Cu-Ni-W	G. H. S. Price, C. J. Smithells and S. V. Williams, *J. Inst. Metals* **62,** 239 (1938).
Cu-Pb-W	Bernoulli, *Pogg. Annalen* **111,** 573 (1860). Sargent, *J. Amer. Chem. Soc.* **22,** 783 (1900). Inouye, *Mem. Coll. Sci. Kyoto* **4,** 43 (1920).
Fe-Mn-W	Barrett, Brown and Hadfield, *Proc. Roy. Soc.* **69,** 480 (1902).
Fe-Ni-W	K. Winkler and R. Vogel, *Arch. Eisenhuttenwesen* **6,** 165 (1932).
Fe-Si-W	R. Vogel and H. Topker, *Arch. Eisenhuttenwesen* **13,** 183 (1939).
Fe-Ti-W	Hamilton and Smith, *J. Amer. Chem. Soc.* **23,** 151 (1901). R. Vogel and R. Ergang, *Arch. Eisenhuttenwesen,* **12,** 149 (1938).
Ni-Cu-W	Roberts-Austen, *Proc. Roy. Inst.* **14,** 497 (1893–95). Irmann, *Metall. und Erz.* **14,** 21, 37 (1917); *Chem. Zentr.* **1,** 1069 (1917).
Pb-Sb-W	H. Falkenberg, German Patent 299,052 (1914).
Ag-Au-Ni-W	G. Fuchs, German Patent 304,551 (1918).
Ni-Cu-Zn-W	Dewar and Fleming, *Phil. Mag.* (5) **36,** 271 (1893); **40,** 95 (1895). Fleming, *Pro. Roy. Inst.* **20,** 885 (1896). Irman, *Metall. und Erz.* **14,** 21, 37 (1917).

Index