IC bureau of mines
information circular 8060

VANADIUM

A Materials Survey

By Phillip M. Busch

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

1961

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March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary.

BUREAU OF MINES
Marling J. Ankeny, Director

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OFFICE OF THE DIRECTOR

March 3, 1849

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
WASHINGTON 25, D. C.

Hon. Frank B. Ellis
Director
Office of Civil and Defense Mobilization
Washington 25, D.C.

Dear Mr. Ellis:

In accordance with the agreement of April 15, 1955, between the Department of the Interior and the Office of Civil and Defense Mobilization, which assigned responsibility to Interior for preparation and revision of Surveys covering 45 mineral commodities, the Bureau of Mines has prepared and herewith transmits to you VANADIUM, A Materials Survey.

Sincerely yours,

Marling J. Ankeny
Director

Foreword

Materials Surveys are prepared to bring into single documents fundamental data on strategic and critical materials needed for military and civilian consumption. These surveys summarize the supply-demand position of the United States with respect to certain essential minerals and metals. They include pertinent information on resources, mining, milling, metal and alloy processing centers, properties of the commodity, principal compounds, alloys, and end-use patterns. In addition, data are presented on the structure of the industry and Government controls, and special information is given for specific commodities.

The Materials Survey on Vanadium was prepared in the Division of Minerals under the supervision of Henry G. Iverson, former chief, Branch of Ferrous Metals, and Frank J. Cservenyak, chief, Branch of Ferrous Metals except for the chapters on geology and resources that were written by Richard P. Fischer of the U.S. Geological Survey. The manuscript was reviewed, in whole or in part, by specialists in the industry, the Geological Survey, and the Bureau of Mines.

CHARLES W. MERRILL
Chief, Division of Minerals.

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By

Phillip M. Busch[2]

With Chapters on Geochemistry and Geology of Vanadium, and Resources
By R. P. Fischer[3]

Introduction and Summary

VANADIUM was discovered in 1801 by Andres Manuel del Rio, a professor of mineralogy at the School of Mines in Mexico City. Del Rio called the new element erythronium. Later, he decided that this was not a new element but a form of chromium. Not until 1831 did Nils G. Sefström, a Swedish chemist, positively determine that the metal was a new element which he named vanadium, after Vanadis, the Scandanavian goddess of beauty. From 1831 to the 1860's and 1870's, the comparative scarcity and high cost of vanadium restricted its commercial use. Shortly after 1870, more information was obtained on the physical and chemical properties of the element. Thereafter, research on vanadium has dealt largely with its use as an alloying element in steel and nonferrous metals.

Vanadium is a widely distributed element in the earth's crust. It is more abundant than many metals but is disseminated in small quantities throughout a great variety of rocks. Relatively few deposits have contained ore of a grade suitable to warrant development for vanadium alone. It is produced in conjunction with uranium, iron, titanium, aluminum, and lead-zinc ores.

The center of vanadium mining in the United States is the Colorado Plateau—the "Four Corners" area of Arizona, Colorado, New Mexico, and Utah—where vanadium is produced as a coproduct of uranium.

Other free world centers of vanadium production are at Otanmäki, Finland, the Otavi Region of South-West Africa, and in the Province of Transvaal, Union of South Africa. Many of the Western European nations, such as the Federal Republic of Germany, France, the Benelux countries, and Italy have derived part of their vanadium supplies either from steel-plant slags or red muds in the Bayer process of aluminum extraction.

Free world vanadium reserves are in the vanadium-bearing sandstones of the Colorado Plateau of the United States; the lead vanadate deposits of South-West Africa; and the titaniferous magnetite deposits of Otanmäki, Finland, and Transvaal, Union of South Africa. Vanadium sulfide deposits of Peru, which supplied the world with vanadium ore and concentrate for many years, have been shut down but remain potentially important as a source of vanadium.

Because vanadium is so widely disseminated in the crust of the earth, there are many other potential sources of vanadium which at present are not of commercial value. These include phosphate rock, vanadiferous shales,

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[1] Work on manuscript completed August 1960.

[2] Physical scientist, Bureau of Mines.

[3] Geologist, Geological Survey, U.S. Department of the Interior.

iron ore, magnetite beach sands, chromite ore, and vanadium-bearing ash and soot retrieved from coal and petroleum.

After domestic vanadium ore is processed in the extractive circuits of mills, the first product made is vanadium pentoxide (red cake) which is subsequently fused in a furnace to produce black oxide. This product normally contains 85 to 92 percent V_2O_5 and is the main raw material used in manufacturing vanadium ferroalloys and compounds.

The largest domestic use of vanadium is in the manufacture of steel because of its grain refining and alloying effects. Ferrovanadium is the major product used for this purpose. Vanadium oxide, ammonium metavanadate, and other forms of vanadium have minor uses compared with ferrovanadium but are of great importance to the chemical and related industries.

Demand for several new vanadium products is increasing. Among these products are a vanadium metal of 99.5 percent purity used for making wire sheet and other special purposes and several grades of vanadium-aluminum utilized in manufacturing titanium metal alloy.

Vanadium metal and vanadium-base alloys possess properties which make promising their use in specialized construction. Among vanadium's favorable characteristics are: Good corrosion resistance to salt water and certain inorganic acids; a low neutron-capture cross section, which has led to its use in atomic reactors; ductility in fabricating operations; and ease of reduction to its compounds compared with more reactive metals such as zirconium and titanium. Metal suitable to serve as the base for alloys containing 10 to 50 percent of other elements can be produced by controllable and relatively inexpensive pyrometallurgical methods. Other binary and ternary alloys containing vanadium as the major element combined with 20 to 50 percent titanium and third element additions of chromium, aluminum, and silicon have high strengths at temperatures from 900° to 1,200° F. and may be applicable to aircraft use.

Domestic mine production of vanadium in ores and concentrates has increased over the years and reached a peak of 7,392 short tons in 1959. The recoverable vanadium content was about 3,719 short tons. Total domestic production of vanadium pentoxide (V_2O_5) in 1959 from domestic and foreign ores and concentrates was 7,305 short tons of V_2O_5 containing 4,092 tons of vanadium.

Ferrovanadium is produced in the United States principally by two companies, Vanadium Corp. of America and Union Carbide Metals Co.

Free world production of vanadium in ores and concentrates is limited to relatively few nations. Of the total world production of 5,325 short tons of recoverable vanadium in 1959, the United States produced about 70 percent; South-West Africa, about 13 percent; Finland, about 10 percent; Transvaal (Union of South Africa), about 6 percent; and Angola, less than 0.5 percent.

Consumption of vanadium in the United States in 1959 was 1,891 short tons. This figure is believed to be about 90 percent of total consumption, which was estimated at 2,101 tons in 1959. Of this total, 79 percent was consumed as ferrovanadium, 8 percent as oxide, 6 percent as ammonium metavanadate, and 7 percent in other forms.

Domestic consumption by uses was as follows: High-speed steel, 22 percent; other alloy steel, 61 percent; alloy cast iron, 1 percent; nonferrous alloys, 6 percent; chemicals, 7 percent; and other uses, 3 percent.

The three principal vanadium products used by industry are: (1) Vanadium oxide, (2) ferrovanadium, and (3) ammonium metavanadate.

Vanadium pentoxide is available commercially in three grades: Fused technical oxide, containing 86 to 92 percent V_2O_5; air-dried technical oxide, containing 82 to 85 percent V_2O_5; and high-purity (c.p.) air-dried oxide, containing about 99.5 percent V_2O_5.

Ferrovanadium, an alloying agent, is made in six grades ranging in vanadium content from 35 to 80 percent. Most ferrovanadium averages 55 percent vanadium, and demand for ferrovanadium with 70 to 80 percent vanadium is appreciable. Silicon content of ferrovanadium ranges from 1.25 to 11 percent, whereas the carbon content ranges from 0.2 to 3 percent. For special requirements, silicon and carbon content can be regulated to meet specifications.

Ammonium metavanadate, a vanadium salt, is usually supplied as a technical grade containing not less than 99 percent NH_4VO_3.

Vanadium oxide is used to add vanadium to steels under special conditions. Ammonium metavanadate and vanadium oxide are used as catalysts, for coloring glass and ceramics, for driers in paints and inks, and for a bleaching medium in processing colored films.

Ferrovanadium, the most important vanadium product used in producing steel, is usually made by reducing fused vanadium pentoxide and iron by the thermit process or in the electric furnace with silicon, ferrosilicon, or carbon.

Vanadium is used in steel for its grain-refining and alloying effects, which increase tensile and torsional strength, toughness, and resistance to abrasion.

Most steels in which vanadium is used as an alloying element require only a few pounds per ton. Although vanadium can be used successfully unalloyed for some applications, it is usually alloyed with chrome, nickel, manganese, tungsten, boron, and titanium.

In addition to vanadium oxide, ferrovanadium, and ammonium metavanadate, several new items are being supplied in limited quantities by producers. Among the newer products on the market are a vanadium metal containing about 90 percent vanadium, which is used as an additive, and a high-purity metal containing approximately 99.5 percent vanadium, which is used in special applications and for research.

Vanadium ore and concentrate, as well as flue dust and boiler scale containing vanadium, enter the United States duty free. The duty on ferrovanadium and alloys is 12½ percent ad valorem. For vanadic acid, vanadic anhydride, salts and compounds, and mixtures of vanadium, the duty is 40 percent ad valorem.

The classification of imports of vanadium products, which includes metals and manufactures, is covered in numerous paragraph and "basket paragraphs" of the U.S. Tariff Commission regulations. These import regulations cover various alloys containing vanadium, cutting tools, fabricated materials, and other products. Most of the import regulations are expressed in percent ad valorem, but for vanadium imported and used as an alloying material in excess of 0.1 percent the import rates is expressed in cents per pound of alloy content.

Quoted prices of the main vanadium raw materials and products in 1959 were: Ore, 31 cents per pound of V_2O_5 contained; vanadium pentoxide, Technical grade $1.38; ferrovanadium, $3.20, $3.30 and $3.40 (Open Hearth, Crucible, and Primos) ; and vanadium metal for remelting, $3.65.

Vanadium compounds are now used almost exclusively as a catalyst in manufacturing sulfuric acid. Platinum, once used for this purpose, could be reestablished as a catalyst in making this important product.

CHAPTER 1. PROPERTIES, PRODUCTS, AND USES

PROPERTIES

Vanadium metal, in the form of ductile shot (99.3 to 99.8 percent V) was produced by J. W. Marden and M. N. Rich as early as 1927 (*149*).[3] They reduced vanadium pentoxide in a steel bomb, using calcium chloride as a flux. Two other scientists, R. K. McKechnie and A. U. Seybolt, improved on the Marden and Rich process. By substituting iodine as a thermal booster for calcium chloride and using excess calcium, they produced a fluid slag which allowed practically all the reduced metal to collect as ductile vanadium of approximately 99.5+ percent purity. The purity of the metal could be raised by resmelting in a vacuum or controlled atmosphere. Methods of producing pure vanadium have since been improved, but metal of the same chemical composition and physical characteristics has been difficult to reproduce. Some physical properties of vanadium metal, as recorded in various publications, are given in tables 1, 2 and 3. Although most published tables agree on the physical and chemical properties of vanadium metal, there is one notable exception. This exception is the melting temperature of the metal. Most tables give this temperature as 1,710° ± 10° C., which was probably based upon early investigations of vanadium metal containing several percent carbon. Some publications of the 1950's give 1,900° ± 25° C. as the melting point of vanadium. The higher purity of vanadium metal now available for testing purposes may be responsible for the large difference in the reported melting temperature.

The tensile properties and hardness of vanadium metal vary with the treatment; vanadium base alloys also exhibit marked differences in physical properties. Much information is needed to supplement that already known on vanadium metal, and a broad field of investigation lies open in the search for binary and ternary alloys.

Vanadium is one of the transition metals of group V of the periodic system (*149*). Transition elements not only have the properties shown on the periodic chart but also many more. The exceptional ability of vanadium to form interstitial compounds with nonmetallic atoms is of interest to metallurgists. Examples are carbides, hydrides, nitrides, and oxides.

TABLE 1.—*Physical properties of vanadium metal (79,92,95,149)*

Atomic number	23.
Atomic weight	50.95.
Crystal structure	Body centered cubic.
Lattice constant	3.0338.
Density . . . grams per cubic centimeter	6.11.
Melting temperature ° C.	1,900 ± 25.
Boiling temperature ° C.	3,000.
Volatility at melting temperature	Very low.
Specific heat (20°–100° C.) calorie per gram	0.12.
Electrical resistivity (20° C.) microhm per centimeter	24.8.
Temperature coefficient of resistivity	0.00280.
Magnetic susceptibility centimeter-gram-seconds	1.4 x 10^{-6}.
Recrystallization temperature to 75 percent cold work ° C.	650–850.
Thermal expansion (microinches per inch per ° C.):	
23° to 100° C.	8.3.
23° to 500° C.	9.6.
23° to 900° C.	10.4.
23° to 1,100° C.	10.9.

TABLE 2.—*Corrosion resistance of vanadium metal (79)*

Corrodent [1]	Corrosion rate, as rolled [2]	Annealed per month, inch [3]
10 percent HCl, 70° C., aerated	0.00072	0.00073
20 percent HCl, 70° C., aerated	.0071	.0045
20 percent HCl, 70° C., air-free	.0123	.0055
37 percent HCl, R.T., nonaerated	.0029	.0026
10 percent H_2SO_4, 70°C., aerated	.00065	.00059
10 percent H_2SO_4, 70°C., air-free	.00036	.00036
10 percent H_2SO_4, boiling	.0048	.0036
85 percent H_3PO_4, boiling	(4)	(4)
Diluted or concentrated HNO_5	(4)	(4)
5 percent $FeCl_5$ plus 10 percent $NaCl$	.072	.075
20 percent $NaCl$ spray	(5)	(5)
Salt water	....	(5)

[1] Aerated: Air bubbled through solution. Air-free: Nitrogen bubbled through solution. Nonaerated: Quiet solution, not saturated with either air or nitrogen.
[2] Hardness: Rockwell C–27.
[3] As rolled metal held ½ hours at 1,650° F. in a vacuum: hardness, Rockwell B–93.
[4] Dissolved.
[5] No effect.

Vanadium compounds and chemicals are catalysts in many processes ranging from those used in the petroleum industry to those used in making organic chemicals and synthetic fibers.

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[3] Italicized numbers in parenthesis refer to items in the bibliography at the end of this report; items are listed chronologically. Page references refer to page in the items and not in this report.

TABLE 3.—*Tensile properties and hardness of vanadium metal (79)*

Condition	Property limit, pounds per square inch	Yield strength, pounds per square inch	Tensile strength, pounds per square inch	Elongation in 2 inches, percent	Rockwell hardess
Annealed 1 hour, 1,500° F.	61,000	76,000	81,000	7	B-76
Cold rolled, 60 percent	63,000	101,000	107,000	1 to 2.5	B-92
Cold rolled, 75 percent	68,000	110,000	117,000	1 to 2.5	B-95
Cold rolled, 80 percent	69,000	142,000	155,000	1 to 2.5	C-29

PRODUCTS AND PREPARATION PROCESSES

In the processing of domestic vanadium ore and concentrate to a marketable form, the first step is to convert the vanadium in the ore to vanadium pentoxide. This product normally contains about 85 to 92 percent of V_2O_5 and serves primarily as the raw material in manufacturing ferrovanadium, vanadium alloys, vanadium metal, and ammonium metavanadate.

Vanadium in the form of the ferroalloy (ferrovanadium) accounts for more than 70 percent of the vanadium consumed yearly.

FERROVANADIUM

Vanadium is ordinarily added to iron and steel as ferrovanadium, of which eight grades are available commercially. Each grade or type of ferrovanadium has a definite carbon and silicon content especially adapted for different requirements in steel making. Table 4 gives the forms of ferrovanadium produced by the major concerns making vanadium products. Vanadium added to steel as ferrovanadium improves certain physical characteristics of the steel.

In the open hearth, ferrovanadium is added to the ladle; in the electric furnace, it is added to the furnace before tap or to the ladle. In either case, it follows additions of other elements in the manufacture of alloys.

Ferrovanadium is used in steelmaking for two distinct purposes (*66*): (1) To refine the grain structure of the steel; and (2) because of the behavior of vanadium carbide, especially its stability at elevated temperatures and its solution in, and separation from, the metallic matrix of steel. The presence of vanadium carbide increases the hardening range of low-alloy steels.

The tendency of vanadium to form a carbide (V_4C_3) is strong, and vanadium is usually found in this form in steel. Although vanadium is present in steel primarily in the carbide phase, it also forms oxides, nitrides, borides, and silicides.

Vanadium carbide influences the grain refinement of steels, but this effect may also result from oxides and nitrides of the metal. However, the influence of oxides and nitrides is not well established. Vanadium produces fine structures in primary crystallization from melts and in phase transformation during heat treatment of steel. Irrespective of the control of grain size imparted to wrought and cast steels, vanadium produces a fine carbide structure in hypereutectoid steels which influences the arrangement of free carbide after hot working.

Vanadium has greater affinity for carbon than manganese and chromium but not so great as columbium and titanium. Vana-

TABLE 4.—*Composition of commercial ferrovanadium and vanadium metal (147,149)*

Product	Analysis, percent				Sizes supplied		
	V	C	Si	Al	Lump	Crushed	Ground
Ferrovanadium:							
Iron foundry grade	38-42	1.00	7.00-11.00				
Grade A, open hearth	50-55	2.00	7.50		X	X	X
Grade B, crucible	50-55 and 70-80	.50	2.25		X	X	
Grade C, primos	50-55 and 70-80	.20	1.25		X	X	
High-speed	50-55 and 70-75	.20	1.50		[1] X		
Special grade	50-55 and 70-75	.50	1.00			[1] X	
Open-hearth grade	50-55	3.00	8.00		[1] X		
Foundry grade	50-55	3.00	10.00				
Vanadium metal:							
90 percent grade	91.45	.10	.90	1.00		X	X
High-purity (nitrogen 0.06, oxygen 0.15, iron 0.10, and hydrogen 0.010 percent).	99.50	.10				X	X

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[1] Several sizes available.

dium carbide is less soluble in austenite than carbides of manganese and chromium and more soluble than titanium carbide. Vanadium carbide is even less soluble in ferrite than in austenite. However, its rate of solution in austenite and in undissolved vanadium carbide restrains grain growth.

In alloy steel castings, vanadium prevents the formation of hard spots caused by localized martensite. Vanadium performs a similar function in welded steels by preventing embrittlement of the area affected by heat during welding.

Vanadium carbide and probably vanadium nitride and oxide account for the fine austenitic grain of vanadium steels.

VANADIUM METAL

Vanadium is difficult to prepare because of its affinity for oxygen, nitrogen, and other gases at elevated temperatures and its reaction with ceramic materials and metals. Although small quantities of relatively pure vanadium metal are marketed for experimental and special purposes, preparation techniques giving consistent results have only recently been perfected. Vanadium metal now being produced commercially is ductile and capable of being rolled, swaged, extruded, and forged. However, some metal produced still shows an embrittlement characteristic which causes cracking upon rolling and is traceable to small impurities difficult to eliminate. Methods for producing vanadium metal include various sealed-bomb reduction techniques in which vanadium pentoxide or other compounds are reduced to metal.

VANADIUM ALLOYS

Besides ferrovanadium, several alloys are available for making special steels and subsequent fabrication into various vanadium-bearing products. (See table 5.) One of the more common of these alloys is Grainal[4] No. 1 (table 5). This alloy contains 25 percent vanadium. It is used as an intensifier to control and increase the capacity of steel to harden and to improve other important mechanical properties in engineering, structural, and some stainless steels. Another alloy, vanadium-aluminum with 2½ or 5 percent vanadium (table 5), is commonly used to control thermal expansion, grain size, and electrical resistivity of aluminum alloys. Not shown in table 5 are two vanadium-aluminum alloys (an 85 percent vanadium—15 percent aluminum and a 60 percent vanadium—40 percent aluminum alloy) used in manufacturing titanium metal alloy. Table 5 lists other vanadium alloys that have been available commercially.

TABLE 5.—*Composition of commercial grades of vanadium alloys, percent (149)*

Alloy	V	Al	Ti	B	Si	Fe	O	Mn	Cu	Ni
Vanadium Grainal No. 1	25	10	15	0.20	....	....	....	....	....	....
Vanadium-aluminum	2.5	97.5	....	....	....	....	....	....	....	....
Vanadium-aluminum	38–43	56–62	....	....	0.50	0.60	0.15	....	....	....
Vanadium-aluminum	80–85	13–17	....	....	1.00	1.00	.25	....	....	....
Aluminum-iron-vanadium	2.25	75	....	....	....	....	....	....	....	....
Copper-nickel-vanadium	60	....	....	....	....	....	....	....	30	10
Copper-aluminum-vanadium	65	10	....	....	....	....	....	....	25	....
Copper-aluminum-vanadium	20	45	....	....	....	....	....	....	35	....
Copper-manganese-vanadium.	60	....	....	....	....	....	....	15	25	....
Cuprovanadium (mossy shot)	10–15	....	....	....	....	....	....	....	35-90	....
Manganese-vanadium	40	....	....	....	....	....	....	60	....	....
Nickel-vanadium	40	....	....	....	....	....	....	....	....	60
Silicon-vanadium	40	....	....	....	60	....	....	....	....	....

VANADIUM OXIDE

All commercial methods now used for extracting vanadium from ores and minerals recover this element as Technical-grade oxide (V_2O_5). This product is the starting material for all other vanadium products. Subsequent refinement gives several other types and grades of oxide (table 6), depending upon the use for which the product is intended.

Commercial Technical grade V_2O_5 is available in fused form, or air dried for easier dissolving. This grade is used directly in making catalysts and, under some circumstances, in electric-furnace steelmaking. Most of it, however, is converted into vanadium alloys or other chemical forms.

TABLE 6.—*Vanadium oxide and ammonium metavanadate products available commercially (65,149)*

	Approximate composition, percent
Vanadium pentoxide, 99.5 percent grade	99.5
Vanadium pentoxide, Technical grade, fused	90
Vanadium pentoxide, Technical grade, air-dried	85
Vanadium pentoxide, Technical grade, fused	86–89
Vanadium pentoxide, red cake	85
Ammonium metavanadate	99
Ammonium metavanadate, technical	(1)
Ammonium metavanadate, chemically pure	(1)

1 Analysis not available.

AMMONIUM METAVANADATE

This product of refiners and processors has many uses in the chemical industry and is available commercially. Like vanadium

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[4] An alloy containing vanadium, titanium, aluminum, and boron.

oxide, it is used in manufacturing vanadium catalysts; as an ingredient of colored glazes for porcelain enamel and ceramic ware: and as a drier or color fixative in paint, dye, and ink.

OTHER PRODUCTS

Some vanadium compounds other than the commonly used oxides are used widely as catalysts or in preparing catalysts—an important use but one consuming relatively little vanadium. The catalytic behavior of several vanadium compounds is known (*149*) for some processes involving oxidation, dehydrogenation, dehydrocyclization, hydroxylation, hydrogenation, and hydrogenolysis. Other properties of these compounds are not so well known.

The unpaired third electrons of some compounds of vanadium, which give the compounds magnetic properties, probably have some role in catalytic behavior. The exact relation this phenomenon has to catalysis is not precisely known.

A list of commercial vanadium compounds follows *(149)*:

Sodium or potassium ortho-, pyro, meta-vanadates.
Vanadium tetroxide (V_2O_4).
Vanadium trioxide (V_2O_3).
Vanadium tetrachloride (VCl_4).
Vanadium trichloride (VCl_3).
Vanadium dichloride (VCl_2).
Vanadium oxytrichloride ($VOCl_3$).
Vanadyl sulfate V_2, $O_2(SO_4)_2 \, x \, H_2O$.
Vanadyl nitrate $VO(NO_3)_2$.
Vanadyl acetate $VO(C_2H_3O_2)_2$.
Vanadyl oxalate $VO(C_2O_4)_2$.
Vanadium nitride
Vanadium carbide
Vanadates of aluminum, bismuth, calcium, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, zinc, etc., are readily produced in the conventional manner.
Sodium orthovanadate, technical.
Sodium orthovanadate, commercial.
Vanadium chloride, syrupy, technical.
Vanadium chloride, syrupy, chemically pure (c.p.).
Vanadium pentoxide, c.p., yellow, air-dried.
Vanadium sulfate, technical.
Vanadium sulfate, c.p.

USES

The number and uses of vanadium alloys have increased in recent years. Small additions of vanadium to iron and steel products have been found to contribute various valuable properties, such as toughness, uniformity, and carburizing qualities in forgings and springs to higher impact resistance, increased strength in the largest forgings and castings, and reduction of internal defects (*38*). Numerous other beneficial effects usually accompany the presence of a minute quantity of vanadium. These beneficial effects include improved machinability, reduced distortion, simpler heat treatment, better weldability, increased wear resistance, better control and uniformity of hardness penetration and gradient, smoother and better finishes, and reduced flaking or spalling of carburized surfaces.

FERROUS ALLOYS

Tool Steels.—Vanadium is commonly used in tool steels where extreme toughness is required. Ability to withstand pounding, cracking, warping, and elevated temperature is reportedly obtainable by using vanadium in tool steels (*31, 32*).

Carbon-vanadium tool steels are utilized in manufacturing punch and die adapters, bushings, shear blades, blankings, drawing, embossing, notching, perforating, shaving, swaging and knife-edge dies, pilots, pads, punchers for blanking, broaching and clippings, stops, strippers, and various other uses.

High-chromium steel containing vanadium and molybdenum is used for cutting, forming, and drawing dies to be used at extremely high production speeds or to minimize warping and danger of cracking during hardening.

Plain carbon or carbon-vanadium steel is used for cutting butt and lap roller pipe to length. For cutting off ragged ends, rotary pipe cutters usually are used. Carbon-vanadium steel, or sometimes chromium-vanadium steel, is utilized in numerous minor applications around tube mills where resistance to shock is required. Applications in which steel of this type is used include shear blades, grips for threading machines, welding rolls, chisels, and jaws on cold-drawing benches.

Vanadium has been used in most tool steels for many years with molybdenum, chromium, tungsten, or other alloying elements. In high-speed steels, the vanadium content usually ranges from 0.50 to 2.50 percent, although higher and lower percentages are sometimes used. (See table 7.) Alloy steels other than high-speed steels contain 0.20 to 1.00 percent vanadium. Such steels are ordinarily melted in electric furnaces and produced by tool-steel methods to meet special requirements (*114*). Tool steels may be used in hand tools or in a variety of mechanical fixtures for cutting, shaping, forming, and blanking materials at either high temperatures or ordinary room temperatures.

The term tool steel does not include the mass-produced open-hearth steel ordinarily used in manufacturing hammers, picks, files, mining bits, mining cutters, low-alloy die blocks, hollow drill steels, and other types of equipment. Tool steels are made in the form of hot and cold finished bars, forgings, special shapes, drill rod, plate, sheets, tool bits, wire, and precision or sand castings.

According to the American Iron and Steel Institute, tool steels are grouped into six main types:

Water-hardening tool steels.
Shock-resisting tool steels.
Cold-work tool steels.
Hot-work tool steels.
High-speed tool steels.
Special-purpose tool steels.

The types of tool steels containing vanadium (table 8) are usually manufactured in the form of bars, which can be furnished in different cross sections, sizes, conditions, and finishes. Methods of forging and rolling tool steels differ considerably from the methods used with other steels. Many types of tool steels initially can be hot-worked only by forging. Tool-steel bars are commonly hot-rolled or forged from conditioned billets or blooms. It is a general practice to process bars in straight lengths, although small sizes produced by rolling may be obtained in coils.

TABLE 7.—*Identification and type classification of tool steels containing vanadium*

[American Iron and Steel Institute]

Type	Content of identifying elements, percent									
	C	Mn	Si	Cr	Ni	V	W	Mo	Co	Cb
WATER-HARDENING TOOL STEELS — SYMBOL W										
W2	0.60–1.40					0.25				
W3	1.00					.50				
W6	1.00			0.25		.25				
W7	1.00			.50		.20				
COLD-WORK TOOL STEELS — HIGH-CARBON CHROMIUM TYPES — SYMBOL D										
D7	2.35			12.00		4.00		1.00		
HOT-WORK TOOL STEELS — SYMBOL H										
CHROMIUM-BASE TYPES										
H11	0.35			5.00		0.40		1.50		
H12	.35			5.00		.40	1.50	1.50		
H13	.35			5.00		1.00		1.50		
TUNGSTEN-BASE TYPES										
H26	.50			4.00		1.00	18.00			
MOLYBDENUM-BASE TYPES										
H41	.65			4.00		1.00	1.50	8.00		
H42	.60			4.00		2.00	6.00	5.00		
H43	.55			4.00		2.00		8.00		
HIGH-SPEED TOOL STEELS — SYMBOLS T AND M										
TUNGSTEN-BASE TYPES										
T1	0.70			4.00		1.00	18.00			
T2	.80			4.00		2.00	18.00			
T3	1.05			4.00		3.00	18.00			
T4	.75			4.00		1.00	18.00		5.00	
T5	.80			4.00		2.00	18.00		8.00	
T6	.80			4.50		1.50	20.00		12.00	
T7	.75			4.00		2.00	14.00			
T8	.75			4.00		2.00	14.00		5.00	
T9	1.20			4.00		4.00	18.00			
T15	1.50			4.00		5.00	12.00		5.00	
MOLYBDENUM-BASE TYPES										
M1	.80			4.00		1.00	1.50	8.00		
M2	.80			4.00		2.00	6.00	5.00		
M3	1.00			4.00		2.70	6.00	5.00		
M4	1.30			4.00		4.00	5.50	4.50		
M6	.80			4.00		1.50	4.00	5.00	12.00	
M7	1.00			4.00		2.00	1.75	8.75		
M8	.80			4.00		1.50	5.00	5.00		1.25
M10	.85			4.00		2.00		8.00		
M15	1.50			4.00		5.00	6.50	3.50	5.00	
M30	.80			4.00		1.25	2.00	8.00	5.00	
M34	.90			4.00		2.00	2.00	8.00	8.00	
M35	.80			4.00		2.00	6.00	5.00	5.00	
M36	.80			4.00		2.00	6.00	5.00	8.00	
SPECIAL-PURPOSE TOOL STEELS — LOW-ALLOY TYPES — SYMBOL L										
L2	0.50–1.10			1.00		0.20				
L3	1.00			1.50		.20				
L4	1.00	0.60		1.50		.25				

Tool-steel bars may be subject to many operations, including annealing or heat treating; cleaning by pickling, blast cleaning, or other cleaning methods; cold drawing, straightening, centerless grinding, grinding and polishing, and hot rolling or forging.

According to the American Iron and Steel Institute (AISI) tool-steel bars are produced in the following conditions and surface finishes, but all types cannot be furnished in all conditions and surfaces listed.

Condition

1. Hot-rolled or forged (natural).
2. Hot-rolled or forged (annealed).
3. Hot-rolled or forged and heattreated.
4. Cold or hot drawn (as drawn).
5. Cold or hot drawn (annealed).

Finish

1. Hot-rolled finish (scale not removed).
2. Pickled or blast cleaned.
3. Cold drawn.
4. Turned.
5. Centerless ground.
6. Polished tenths.

(Finishes 4, 5, and 6 are applicable only to round bars.)

Table 8 shows a grouping of six types of tool steels and a second classification of tool steels based upon the predominate alloying element, that is, chromium, molybdenum, or tungsten. This identification and type classification of tool steels correlated well with shipments of major types of high-speed and tool steels (table 8) published in the annual statistical report of AISI. From a comparison of these classifications and shipments, methods of fabrication and the importance of each type can be ascertained.

Because of the complexity of the alloy content and the large number of manufacturers of tool steels, it is difficult to systemize all tool steels into a simple table. However, the two classifications of tool steels by AISI presents a simplified guide to the selection and correlation of properties.

Alloy Steel.—The quantity of vanadium added to engineering and constructional steels is generally 0.10 to 0.25 percent (for high-impact steels, only 0.05 to 0.10 percent).

TABLE 8.—*U.S. shipments of high-speed and tool steel (exclusive of hollow drill steel) by major types in short tons*

[American Iron and Steel Institute]

Grade[1]	C[2]	Cr[3]	W[3]	Mo[3]	V	Co	1948	1949	1950	1951	1952	1953	1954	1955	1956	1957	1958
CLASS A — HIGH SPEED (Composition, percent)																	
I	0.60	4.5	6.75	5.50	[3] 2.10	0	5,622	2,540	6,161	19,398	11,821	11,311	6,446	10,504	10,357	7,792	4,868
Ib	.90	4.5	6.75	6.50	[2] 2.25	0	85	104	154	557	549	566	489	847	1,058	1,037	656
Ic	.60	4.5	6.75	5.50	[3] 2.20	[2] 3.5	316	208	572	239	243	85	59	118	146	132	45
II[4]	.60	4.5	2.00	9.25	[3] 1.30	0	1,499	560	1,559	7,504	4,185	5,283	3,222	5,899	5,612	5,283	3,043
IIc[4]	.60	4.5	2.00	9.25	[3] 2.20	[2] 3.5	35	26	42	270	214	176	139	153	232	214	62
III[4]	.60	4.5	0	9.25	[3] 2.20	0	665	151	948	2,421	2,811	3,684	2,443	4,088	3,218	3,242	1,278
IIIc[4]	.60	4.5	0	9.25	[3] 2.20	[2] 3.5	83	29	73	178	25	44	17	7	25	72	....
Total, class A							8,305	3,618	9,509	30,567	19,848	21,149	12,815	21,616	20,648	17,772	9,952
CLASS B — HIGH SPEED																	
IV	0.55	4.5	19.0	0	[3] 1.30	0	7,949	4,041	6,823	6,061	1,601	2,336	1,838	2,366	2,526	1,926	1,098
IVb	.55	4.5	19.0	1.25	[2] 1.75	0	436	391	546	499	204	259	204	284	260	149	98
IVc	.55	4.5	22.0	1.25	[3] 2.20	[2] 3.5	1,071	884	1,026	929	812	841	498	695	828	716	470
Total, class B							9,456	5,316	8,395	7,498	2,617	3,436	2,540	3,345	3,614	2,791	1,666
Total, high-speed tool steels							17,761	8,934	17,904	38,056	22,465	24,585	15,355	24,961	24,262	20,563	11,618
Ratio of class A to total high speed, tool steels, percent							46.7	40.5	53.1	80.3	88.3	86.1	83.5	86.6	85.1	86.4	85.6
OTHER TOOL STEELS																	
V. All hot-work steel							7,127	5,140	8,068	12,995	12,719	14,229	8,857	12,062	14,455	11,924	8,834
VI. High Cr (4 percent minimum) die steel							6,707	4,707	7,168	12,230	9,700	8,619	7,832	10,488	12,161	9,848	7,961
VII. All other alloy tool steels							37,988	26,251	40,891	78,621	57,103	53,257	40,342	52,949	59,859	45,647	34,618
VIII. Carbon tool steels							20,251	12,968	19,038	34,112	20,233	16,941	12,626	15,468	17,420	12,327	8,392
Total, other tool steels							72,073	49,066	75,705	137,958	99,755	93,046	69,657	90,967	103,895	79,746	59,805
Total, all tool steels							89,834	58,000	93,609	176,014	122,220	117,631	85,012	115,928	128,157	100,309	71,423
Ratio of high-speed to total tool steels, percent							19.8	15.4	19.1	21.6	18.4	20.9	18.1	21.5	18.9	20.5	16.2
Ratio of class A high-speed to total tool steels, percent							9.2	6.2	10.2	17.4	16.2	18.0	15.1	18.6	16.1	17.7	13.9

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[1] Prior to July 1, 1951.

[2] Minimum.

[3] Maximum.

[4] Specifications for grades II, IIc, III, and IIIc called for 1.8 percent W and 8.75 percent Mo.

Steels containing more than 0.50 percent vanadium are for special purposes (*65*, pp. 52–57).

Engineering and constructional steels, in heavy and light sections, contain vanadium and other alloying elements. Carbon-vanadium steel has been used by the railroad industry for large forgings. Small heat-treated forgings contain about 0.18 percent vanadium and 0.50 percent carbon, like the large forgings, and have been used in crankshafts of automotive engines. Because of its freedom from warping, vanadium-carbon steel is especially advantageous for this use.

Low-carbon vanadium steel is used for making welding rods for oxyacetylene welding, because the dense, fine-grained structure and great uniformity imparted by the vanadium results in welds possessing high strength and good resistance to impact (*31*).

Where physical properties, such as toughness, hardness, and resistance to wear, are desirable, chrome-vanadium steels may be used with satisfactory results. Low-carbon chromium-vanadium steels are used frequently for case-carburized parts for wrenches, pneumatic tools, pistons, gears, wristpins, camshafts, and many other parts subjected to wear involving high stresses. Chromium-vanadium steels of medium-carbon content are used as gears, axles, steering arms, crankshafts, connecting rods, and valve-operating parts. Ball and roller bearings, dies, wrenches, tools, and wearing plates are made of high-carbon chromium-vanadium steels. Because of their resistance to deterioration when exposed to hydrogen at high temperatures and pressures, chromium-vanadium steels have been used for making high-pressure equipment in the chemical industry (*31*).

Chromium-vanadium steels are used in earthmoving and mining equipment for highly stressed bolts, studs, and pins; cylinders and barrels for pneumatic hammers; clutch gearing; and shafts for steam shovels.

Another group of vanadium-bearing steels is the chromium-vanadium steels that were developed originally to replace certain quenched and tempered carbon and low-alloy steels, whose heat-treating cycle included a drastic quench, often resulting in high scrap loss. Originally these steels, were used in automotive crankshafts and possessed excellent mechanical properties. Steel of this type has since been used for forgings of irregular contours and sections such as camshafts, wheel hubs, eccentrics, and other highly stressed parts. For automotive use, chromium-vanadium steels with special specifications have been developed, known as the SAE–6100 series.

There are now only three SAE (Society of Automotive Engineers) chromium-vanadium steels listed. (See table 9.) The carbon, manganese, phosphorus, sulfur, silicon, chromium, and vanadium content of each steel has a definite range.

SAE–6120 steel responds readily to cyanide casehardening (*33*). It is used for forgings, stampings, gears, bolts, and washers. The nitrides formed in this steel are fine and do not tend to develop a long needlelike structure. This steel has case toughness, but the transition from the hard surface to the core is not abrupt and even prolonged cyaniding does not embrittle the core. The same chromium-vanadium steel is also used in boiler construction, pressure vessels, superheated tubes, bolts, tubing for the chemical industry, and welding rods.

TABLE 9.—*Alloy element content of selected SAE chromium-vanadium steels, percent (146)*

SAE and AISI No.	Alloy element						
	C	Mn	P	S	Si	Cr	V
6118	0.16–0.21	0.50–0.70	0.040	.....	0.040	0.50–0.70	0.10–0.15
6120	.17– .22	.70– .90	.040	0.040	0.20– .35	.70– .90	.10
6150	.48– .53	.70– .90	.040	.040	.20– .35	.80–1.10	.15

SAE–6150 steel is used in manufacturing parts that require high elastic limits and fatigue resisting qualities over a wide range of stresses. This particular steel is used for automotive chassis springs, valve springs, and locomotive and railway-car springs. These steels are also used for welding worn railway rails and provide a tough resistant surface.

Besides the SAE–6150 steel, also known as a spring steel, a silicon-vanadium steel has been used in making springs. Steel of this type possesses free-scaling properties, resulting in good surfaces and mechanical characteristics (*32*).

Several classes of manganese-vanadium steels have been used for various purposes. Vanadium in these steels inhibits grain growth to a marked degree, resulting in a more uniform structure. It also helps to overcome segregation and martinistic formation in manganese steels (*31*).

Manganese-vanadium steel has been used extensively in the railroad industry. Railroad tanks, cars, and other structures are made of steel of this type. This steel has higher strength and ductility in the as-rolled condition and, because of its inherently fine-grained structure and low-carbon content, is particularly adaptable for welding. Welds of this steel retain strength and ductility almost equal to that of the original material and show little tendency toward air hardening. Such steels are also used in shipbuilding.

Other manganese-vanadium steels of slightly higher carbon and manganese content have been used for forgings of small or large cross section. Steels of this type combine a high yield point and ductility with good resistance to impact.

The penetration of hardness of this type of steel is very good, resulting in a uniform hardness throughout large masses (31). Impact strength in manganese-vanadium structural and forging steel is also high and retained even at low temperatures. Such steels are suitable for use outdoors in very cold climates and low temperature processes of various chemical industries.

Alloy Cast Iron.—From 0.10 to 0.15 percent of vanadium increases the strength of cast iron 10 to 25 percent and adds greatly to its toughness (*65*, p. 54). Cast iron containing vanadium has been used in steam-locomotive cylinders, piston bushings, and other parts. Steam-engine parts, especially cylinders, made of vanadium cast iron, greatly outlast those made of ordinary cast iron. Vanadium cast iron has also been used in constructing heads and cylinder linings of large diesel engines.

Cast irons in which vanadium is the only alloying element are utilized primarily in moderately high temperature applications and in heavy sections requiring uniform hardness without brittleness. These uses include locomotive cylinder blocks, grate bars, forming dies, bottle molds, and brass mill rolls.

At present, most cast iron containing vanadium also contains additional alloying elements.

Among the more common types of cast iron are the chromium-vanadium rolls, which contain as much as 2 percent chromium and have been used for many years in steel mills. Recently, chromium-vanadium cast iron in light sections has been utilized for automotive-engine clutch plates. Small quantities of chromium, vanadium, and titanium are added to low-alloy cast iron to produce cast steels with the desired physical characteristics. Still another type of cast iron used in heavy dies for forming and drawing automobile body parts are nickel-irons which have exceptionally good wear-resistant qualities. Nickel-chromium-vanadium cast irons are used for cold-rolling strip, dies, chilled rolls, and similar applications.

Cast irons composed of nickel, molybdenum, and vanadium are noted for their great strength, and vanadium contributes many of the desirable qualities to steel of this type. Metal with this combination of elements has been used for brake drums.

Magnetic Alloys.—Several magnetic alloys containing vanadium have been developed. These alloys are known by the trade names of Vicalloy, Hyperm, Koertit, and Permendur (*149*). Some of these alloys are based on 50 percent cobalt and 2 to 14 percent vanadium.

An improved alloy of excellent formability called Supermendur, which contains 49 percent cobalt, 49 percent iron, and 2 percent vanadium may find use in power transformers, pulse transformers, telephone-receiver diaphragms, switching and memory devices, and magnetic amplifiers. Transformers with cores of this material can improve power output nearly 30 percent over ones of the same size made of other materials. The improved magnetic material used in magnetic amplifiers enables a decrease of about a fifth in size with the same output.

NONFERROUS ALLOYS

Aluminum Alloys.—Several types of commercially prepared alloys containing high percentages of aluminum and vanadium are available for industry. Among these products are the aluminum-vanadium alloys in which the vanadium content is either 2.5, 5, 40, or 85 percent and the remainder is aluminum and fractional percentages of silicon, iron, and oxygen. These alloys are used for control of thermal expansion, grain size, and electrical resistivity and to improve the high-temperature strengths of aluminum and titanium metal alloys. A Grainal alloy containing high percentages of aluminum, vanadium, and various other alloys also is available for various uses. This product, called Grainal No. 1, contains approximately 25 percent vanadium, 10 percent aluminum, 15 percent titanium, and 0.20 percent boron. It is used as a practical and economical intensifier for increasing the capacity of steel to harden and generally improving its physical properties.

Titanium Alloys.—One of the more recent alloy developments has been the discovery and use of titanium-base vanadium alloys. Developments by the Armour Research Foundation, Battelle Memorial Institute, and industrial concerns have yielded some new alloys which may find increasing use and in which vanadium is a minor constituent. These new alloys contain 3.4 to 4.5 percent vanadium and 4 to 6.5 percent aluminum in a titanium base. They are available commercially as forgings, bars, plates, and sheets in limited quantities (*109*). These alloys have usable strength up to 1,000° F., high tensile and impact strengths, and good weldability. Research is continuing on titanium-base alloys. As more is known about the physical metallurgy of these alloys, airframe and engine producers are beginning to include some of these higher strength materials in their designs for certain parts (*118*).

Miscellaneous Alloys.—Copper, vanadium, and vanadium-aluminum alloys are used for aircraft bushings, ships' propellers, and other parts where high strength and resistance to corrosion are needed.

HARD AND SPECIAL MATERIALS

Vanadium carbide (VC) is one of the hard-metal carbides. This monocarbide may be obtained by reacting the vanadium tetrachloride with toluol vapors and depositing the carbide on a hot tungsten filament (*124*). The reaction is carried out between 1,600° and 2,000° C. Vanadium carbide may be prepared with vanadium pentoxide (V_2O_5) and carbon at a carbonization temperature of approximately 3,275° F. (1,816° C.). The product contains 18.97 percent carbon and 0.19 percent graphitic carbon (*137*). Theoretical carbon content of vanadium carbide is approximately 19.08 percent carbon.

Other vanadium carbides corresponding to V_5C, V_4C_3, and V_2C have been reported (*67*). In steels, V_4C_3 may appear (*135*).

Properties of vanadium carbide (VC) have been reported as follows: Hardness, (Mohs') 9–10; electrical resistivity at room temperature, 1.56×10^4 ohm-centimeters; compressive strength at room temperature, 89,000 pounds per square inch; and fabrication method, hot pressing (*142*).

Hard-metal carbides are used in the tool and die industry, for electrolytic electrodes, in gas turbines, and for many other applications. The quantity of vanadium carbide produced and used is not known.

CHEMICALS AND CATALYSTS

Among the earliest references on the use of vanadium compounds in catalysts are those credited to John Lightfoot, who in the 1870's used vanadium salts as oxidation catalysts in the production of aniline black for dyeing and printing (*133*). Various vanadium compounds, such as resinates, nephthenates, and linoleates, have been used as driers in paints and varnishes and in making lusters for pottery, porcelain, and glass for many years.

A review of the literature revealed that vanadium compounds are utilized as catalytic agents in numerous uses significant to many important industrial functions. However, over the years, the quantity of vanadium compounds used by the chemical and related industries has been small compared with metallurgical applications.

Some vanadium compounds of particular importance to the chemical industry are vanadium oxide, ammonium metavanadate, and sodium orthovanadate, which are used as catalysts. Other vanadium compounds used by the chemical industry were listed on page 8.

One of the major uses of vanadium pentoxide is as a catalyst in preparing sulfuric acid, a process developed in Germany. In 1900, E. de Haen obtained a patent covering the use of vanadium as a catalyst in making sulfuric acid. According to the de Haen process, vanadium or its compounds, especially vanadium pentoxide, on asbestos as a carrier was reported to produce sulfuric anhydride at 465° C. with a conversion rate of 84 percent of the sulfur dioxide input. Since this process was developed, no great changes in the principle of the reaction or in the main catalytic agent have been revealed. The rate of conversion has been increased by improvements in equipment resulting in better control. Most of the contact sulfuric acid plants in the United States use vanadium catalysts.

Catalyst manufacturers use either ammonium metavanadate or vanadium pentoxide as a starting material. Although they specify the highest purity and consistency in analyses, products designated as Technical grade are satisfactory for preparing catalysts.

Uses of vanadium compounds as catalysts (*149*) are given in the following list.

Production of sulfuric acid.
Oxidation of benzene to maleic anhydride.
Oxidation of napthalene to phthalic anhydride.
Oxidation of anthracene to anthraquinone.
Oxidation of chlorenated hydrocarbon to maleic and fumaric acid.
Oxidation of acrolein to acrylic acid.
Oxidation of toluene or xylene.
Oxidation of alkenyl and alkyl derivatives of pyridine in presence of ammonia.
Oxidation of amino acids.
Oxidation of cyclohexanal to adipic acid.
Oxidation of naphthalene to 1, 4 naphthoquinone.
Ammonia synthesis.
Hydrogenation of carbon monoxide.
Dehydration of organic acid to ketones.
Dehydrocyclization of paraffins to aromatics, such as hexane to benzene.
Dehydrogenation of butane to butenes.
Dehydrogenation of butenes to butiadiene.
Oxidizing agent in the formation of various shades of aniline dyes.
Catalyst in petroleum cracking.

Catalyst granules average about 7 percent vanadium pentoxide by weight and are deposited on a carrier such as silica gel or magnesium silicate. In the United States, the average converter contains about 230 pounds of catalyst or 16 pounds of vanadium pentoxide per ton of daily sulfuric acid capacity. A 6-percent-a-year replacement of catalyst is considered normal; however, some manufacturers replace catalysts every 2 or 3 years. Owing to differences in raw materials and resulting impurities in feed gases, the life of catalysts may vary greatly. There is probably little reworking of "spent catalysts" in this country.

Vanadium catalysts are also used in the production of other organic compounds, such as phthalic and maleic acids and anhydrides. Phthalic anhydride produced with a vanadium catalyst, in turn, serves as the basic raw material for making many products, including alkyd resins and plasticizers for vinyl and nitrocellulose resins. Alkyd resins are used in manufacturing surface coatings and paints. Cellulose and vinyl resins are used to make many products ranging from flooring to drapery fabrics.

A related derivative of phthalic anhydride, dimethyl phthalate, is used in manufacturing insect repellents and films. Terephthalic acid is used in the production of synthetic fibers with ethylene glycolterephthalate.

Anthraquinone is produced from phthalic anhydride by the Friedel-Crafts reaction. It is a starting material for manufacturing dyes, especially khaki. During World War II, anthraquinone was made from anthracene or benzaldehyde by vapor-phase oxidation using a vanadium catalyst. Phthalic acid is used in preparing benzoic acid and, with benzoates, is used in the fruit industry as a preservative and in the manufacture of paints and lacquers.

Phthalic acids and anhydrides were produced from napthalene by oxidation over a vanadium catalyst. As the oil industry was left with excess xylene after the war, plants were established for converting xylene to phthalic acids or anhydrides. These plants also used a vanadium catalyst.

Many modifications of the original patent by Gibbs and Conover (1917) utilizing fused vanadium pentoxide have been developed. In this process, alundum or silica gel may be used as a carrier. Granular material of controlled size has been utilized in fluidized-bed operations, and pelleted products have been used in fixed-bed converters. Under normal operating conditions, modern catalysts can last 6 years or more. Yields may run as high as 95 percent.

The conversion process is carried out at 300° to 500° C., depending upon the type of catalyst. Contact time may range from approximately 0.2 to 0.5 second with an air-to-hydrocarbon ratio of 3 to 10 times the theoretical ratio. Because the reaction is exothermic, converters are usually provided with cooling arrangements. Normally, phthalic anhydride is produced in a single-pass operation. Long contact times favor the formation of maleic anhydride and advanced oxidation products. Lower oxidation products, such as aldehydes, result from short contact times.

It has been estimated that 30 to 55 pounds of V_2O_5 is needed per million pounds of annual phthalic anhydride capacity. An initial charge, however, will require about 160 pounds of V_2O_5 per ton of daily capacity. On an annual basis, 200 pounds of V_2O_5 is required per million pounds of phthalic anhydride capacity.

Maleic anhydride is another raw material of importance in the manufacture of resins and plastics. In the process described by Weiss and Downs in 1920, it is produced by introducing a mixture of air and benzene at 400° to 450° C., under a pressure of 1 to 3 atmospheres, into a converter where the gaseous mixture contacts V_2O_5 or $V_2O_5MoO_3$. These catalysts are mounted on an inert carrier, such as alumina, aluminum turnings, silica, or diatomite. The contact time is 0.1 second at 1 atmosphere of pressure with a feed of approximately 210 to 560 cubic feet of air for each pound of benzene. The vapors, after reacting with the catalyst, are cooled to about 60° C.; at this temperature most of the anhydride and acids condense and the rest of them are absorbed and recovered in water or in an organic solvent. The products resulting from this reaction include maleic anhydride, maleic acid, smaller quantities of fumaric acid, some benzene, and some water and CO_2.

Because of the large quantities available, maleic anhydride is the basic raw material for many organic compounds. It is used for making alkyd coating resins, polyester coating resins, low-pressure laminates, drying oils, agricultural chemicals including pesticides, soil conditioners and plant growth regulators, and plasticizers. Trends in the manufacture of boat hulls, automobile bodies, and other consumable items may greatly expand the markets for plastics.

Vanadium catalyst requirements probably range from 75 to 120 pounds per million pounds of maleic anhydride.

Catalytic oxidation of cyclohexanol or cyclohexanone with nitric acid in the liquid phase produces adipic acid. This reaction, which may occur at temperatures ranging from 35° to 275° C., is usually catalyzed by ammonium metavanadate. Most of the catalyst is not recovered and is probably lost in the mass reaction.

The acid is used with hexamethylenediamine to produce nylon.

Niacin or nicotinic acid is important as an antipellagra agent. Nicotine has been oxidized to nicotinonitrile by passing nicotine vapors and 30 to 60 times their weight of air at 450° C. over a vanadium catalyst. Subsequent heating with a mineral acid produces nicotinic acid.

Besides the current industrial uses for vanadium catalysts, many potential applications have been suggested. Vanadium has been mentioned for use as a catalyst in power generation by turbines. A hydrocarbon fuel is oxidized with the aid of a catalyst by a gas mixture adjusted to keep oxygen between 2 and 5 percent at a temperature ranging from 500° to 800° C. under a pressure of 12 to 60 atmospheres. The resultant hot gases drive a turbine; part of the gas is recirculated, and part is used to drive a compression turbine. Vanadium is capable of catalyzing this reaction. The low operating temperature of such a turbine prevents many problems common to ones which operate at higher temperatures.

A similar application that has been proposed is to catalyze the rapid evolution of high-temperature gases from solid nitroguanidine, using vanadium pentoxide, molybdic acid, or cerium dioxide. These catalysts insure complete burning of the gas-generating material, which in turn produces high pressure and temperatures between 900° and 1,000° C.

Another proposed idea is the dehydrogenation of hydrogen sulfide and the production of elemental sulfur using a vanadium catalyst. This process might be used in treating sour gas and sour feed stock in petroleum refining.

Many patents issued to petroleum companies describe the use of vanadium catalysts in refining and re-forming petroleum and in petrochemical production, but the petroleum industry does not appear to be using them in their operations.

Patent literature also discloses references to the application of vanadium catalysts in polymerization, dehydrogenation, dehydration, and other classes of reactions. Oxidation reactions, such as acrolein to acrylic, acetylene to acetaldehyde, acetaldehyde to acetic acid, and methanol to formaldehyde, have been accomplished with vanadium catalysts, but their economic utilization is not certain owing to other established practices. A bibliography (*149*), assembled by C. M. Cosman (metallurgical engineer, Vanadium Corp. of America), compiled from entries in Chemical Abstracts, 1940–54, gives the type designation of the reaction, a description of the reaction, the catalyst used, and the observer and source of information.

Glass and Ceramics.—Vanadium acts much like chromium as a glass colorant. Minute quantities of V_2O_5 in different-base glasses give colors ranging from almost colorless through various shades of green, yellow, tan, amber and gray. Vanadium usually causes green tints owing to the superposition of the green of trivalent vanadium and the yellow of pentavalent vanadium. A large excess of alkali leads to the formation of colorless vanadates. Under special conditions, solarization may be used to develop the lavender color of bivalent vanadium.

Vanadium has been the least used of eight transition elements in the first long series of the periodic chart which gives the fundamental glass coloring agents. The reason advanced for the infrequent use of vanadium is that the greenish color, which it ordinarily produces, may be obtained more economically with iron, copper, or chromium or with various combinations of these metals and their derivatives (*34*). Special applications of vanadium may lead to greater interest in its use as a colorant when more information is available about the chemistry of glass technology.

The reaction of coloring agents in glass manufacture is related to the influence of melting conditions and composition. Table 10 gives several series of base glasses in which enough vanadium pentoxide was added to the batch to give 1 percent of V_2O_5 in the final glass. The colors vary greatly, which is significant. A more important use of certain colored glasses is in the measurement of ultraviolet intensities for climatological purposes.

Glass prepared with small amounts of vanadium and cerium have a green color owing to the V_3+. Cerium dioxide introduced into glass gives off oxygen to form the trivalent oxide. At low temperatures, this trivalent cerium shows a strong tendency to revert to its original tetravalent state. In the presence of trivalent vanadium, the following reaction seems to take place:

$$\mathrm{Ce}^{+++} + \mathrm{V}^{+++} \longrightarrow \mathrm{Ce}^{++}_{++} + \mathrm{V}^{++}.$$

Such a reaction requires a rather high activation energy and will not take place under ordinary conditions. In the presence of ultraviolet light, the cerium absorbs ultraviolet light quanta and becomes activated, which causes the reaction to take place. This discoloring or solarization occurs under the influence of sunlight, and the color changes from faint green to pink. The cerium-vanadium reaction is very sensitive, and on a bright summer day the color change may be noticeable in less than 1 hour with glass having the proper proportions of these two elements.

In the pentavalent state, vanadium is used in clear glass to absorb ultraviolet rays. When vanadium is present as V_2O_3, a rich green color is produced but the glass does not absorb the ultraviolet rays (*149*). The addition of metal vanadate to glass produces different colors, depending upon the type of glass and on furnace conditions. Oxidizing conditions will yield yellow to brown to violet colors, whereas reducing conditions will form green glass. The range of color for a few vanadates is as follows: Cobalt vanadate, green to blue; copper vanadate, yellow-green to blue-green; manganese vanadate, yellow-green to amber to wine red; and nickel vanadate, yellow-green to deep violet. Combinations of various metallic vanadates will yield many useful colors.

TABLE 10.—*Colors produced by 1 percent V_2O_5 in various base glasses (34)*

Base glass composition:	*Color*
$Na_2O, CaO, 6SiO_2$	Mint green.
$K_2O, CaO, 6SiO_2$	Do.
$Li_2O, 2SiO_2$	Weak yellow.
Na_2O, SiO_2	Colorless.
$Na_2O, 2SiO_2$	Weak yellowish green.
$Na_2O, 3SiO_2$	Green.
$Na_2O, 3\frac{1}{2}SiO_2$	Do.
$Na_2O, 4SiO_2$	Do.
K_2O, SiO_2	Light yellow.
$K_2O, 2SiO_2$	Nearly colorless.
$K_2O, 3SiO_2$	Light green.
$K_2O, 4SiO_2$	Mint green.
B_2O_3	Tan (gray).
$Li_2O, 3B_2O_3$	Yellow green.
$Li_2O, 4B_2O_3$	Do.
$Li_2O, 5B_2O_3$	Amber (gray).
$Na_2O, 2B_2O_3$	Greenish yellow.
$Na_2O, 3B_2O_3$	Weak green.
$Na_2O, 4B_2O_3$	Do.
$Na_2O, 5B_2O_3$	Amber (gray).
$K_2O, 2B_2O_3$	Colorless.
$K_2O, 3B_2O_3$	Bright green.
$K_2O, 4B_2O_3$	Gray-green.
Na_2O, P_2O_5	Dark brown.
$Na_2O, 3P_2O_5$	Bright green.
$Na_2O, \frac{1}{2}MgO, P_2O_5$	Do.
$Na_2O, \frac{1}{2}CaO, P_2O_5$	Amber.
$Na_2O, \frac{1}{2}ZnO, P_2O_5$	Do.
$Na_2O, \frac{1}{2}SrO, P_2O_5$	Yellowish green.
$Na_2O, \frac{1}{2}BaO, P_2O_5$	Green.
$Na_2O, \frac{1}{2}PbO, P_2O_5$	Dark amber.
$Na_2O, \frac{1}{2}MgO, 2B_2O_3$	Weak yellow.
$Na_2O, \frac{1}{2}CaO, 2B_2O_3$	Do.
$Na_2O, \frac{1}{2}ZnO, 2B_2O_3$	Do.
$Na_2O, \frac{1}{2}SrO, 2B_2O_3$	Do.
$Na_2O, \frac{1}{2}BaO, 2B_2O_3$	Do.
$Na_2O, \frac{1}{2}PbO, 2B_2O_3$	Do.
$Na_2O, \frac{1}{2}MgO, SiO_2$	Yellowish green.
$Na_2O, \frac{1}{2}CaO, SiO_2$	Lighter yellowish green.
$Na_2O, \frac{1}{2}ZnO, SiO_2$	Do.
$Na_2o, \frac{1}{2}SrO, SiO_2$	Do.
$Na_2O, \frac{1}{2}BaO, SiO_2$	Least color.
$Na_2O, \frac{1}{2}Pb, SiO_2$	Greenish yellow.
Na_2O, SiO_2	Colorless.
$Na_2O, SiO_2+0.3B_2O_3$	Do.
$Na_2O, SiO_2+0.6B_2O_3$	Weak yellowish green.
$Na_2O, SiO_2+0.9B_2O_3$	Greener.
$Na_2O, 2SiO_2$	Weak yellowish green.
$NA_2O, 2SiO_2+0.3B_2O_3$	Weak green.
$Na_2O, 2SiO_2+0.6B_2O_3$	Green.
$Na_2O, 2SiO_2+9B_2O_3$	Dark green.
$Na_2O, 2SiO_2$	Weak yellowish green.
$Na_2O, 2SiO_2+0.01P_2O_5$	Yellowish green.
$Na_2O, 2SiO_2+0.06P_2O_5$	Bluish green.
$Na_2O, 2SiO_2+0.5P_2O_5$	Bright green.

Compounds of vanadium are used in the ceramic industry for glazes and enamels. Zirconia, with silica and vanadium pentoxide, produces blue to bluish-green color. Vanadium yellow is produced by heating lead oxide with vanadium salts and zirconia. A yellow fluorescent product is produced by zinc oxide and vanadium pentoxide. Vanadium oxide and pentoxide produce a stable yellow color which can be utilized for glaze, underglaze, or body stain. Cadmium sulfide, with selenium and vanadium compounds, produces a bright red color. Vanadium compounds in paint and varnish promote rapid drying and produce a tough, uniform, wrinklefree film.

Vanadyl linoleate, oleate, palmitate, phenolate, stearate, and resinate are some of the metallo-organic compounds that can be made. Increasing research on the chemistry of vanadium should create an even greater demand for vanadium chemicals.

Photography.—One of the vanadium salts, vanadium chloride, has been used in photographic processes for toning silver bromide prints, imparting a green color (*108*). According to U.S. Patent 979,887, issued in 1910, toning is achieved by mixing 500 grams of liquid vanadium chloride with 1,300 grams of anhydrous oxalic acid; compressing the product into tablets; and preparing toning baths by dissolving 3.8 grams of this product, 1.5 grams of anhydrous oxalic acid, 1 gram of ferric oxalate, and 1 gram of potassium ferricyanide in 1 liter of water.

Therapeutic Purposes.—The therapeutic effects of vanadium compounds in pharmacy have not been fully investigated. Compounds of vanadium have been used in minute quantities to achieve diverse therapeutic effects (*106*). Vanadium used in medicine must be present as a stable neutral compound with a minimum of toxicity. It has been used as an antiseptic and inhibitor of germ growth. An example is the use of vanadium oxytrichloride in a strong solution of sodium chlorate to treat abscesses, infected wounds, open sores, and ulcers. Vanadium compounds have also been used: (1) As a chemotherapeutic agent in gastric catarrhs; (2) to destroy fermentation microbes without impeding the digestive enzymes; (3) to inhibit the growth of organisms, such as spirochetes and pneumococci, which are now treated with antibiotics; (4) as a catalyst or oxygen promoter to counteract the deficiency of hemoglobin in anemias and to assist the defensive mechanism in infections, such as influenza or pneumonia; and (5) to boost appetite and improve nutrition and general resistance.

Another reference (*15*) lists additional vanadium compounds used for therapeutic purposes, including vanadic acid, sodium metavanadate, iron metavanadate, and lithium metavanadate.

In European countries several vanadium compounds have been used to treat numerous human ailments, but in the United States their therapeutic applications have been limited because they lack pharmacopoeial recognition. However, research on the use of vanadium compounds continues. Studies on the use of vanadium salts were conducted recently by research teams at the University of Kansas Medical School (*141*). According to the theory advanced by scientists of this institution, vanadium salts tend to reduce deposits or discourage the production of cholesterol, a fatty substance which blocks arteries in the body.

SUBSTITUTE MATERIALS

Supplies of vanadium have been ample to meet requirements in the United States. At present, production is in excess of domestic requirements, and vanadium raw materials and products are being exported to foreign nations. It is only necessary to resort to substitutes when, as in 1941–43, apparent scarcity of vanadium was caused primarily by substituting steels containing chromium and vanadium for unattainable nickel steels. Equally serviceable substitutions for vanadium steels were molybdenum or molybdenum-silicon steels with a grain-refining addition of aluminum. During World War II, vanadium was omitted from rolled tank armor. The Navy used manganese-titanium steel for high-strength plate in place of steel containing vanadium.

Platinum may be used as a substitute for vanadium as a catalyst.

CHAPTER 2. HISTORICAL BACKGROUND

DISCOVERY

For 100 years after vanadium became known to the world, it was mainly a curiosity to scientists and scholars. Vanadium was considered a rare metal, and for many years ores that contained vanadium were of interest only to collectors of minerals (*57*). The metal has risen from a position of comparative obscurity to one of importance as an alloying element and as a constituent in chemicals. Like many other ferroalloy metals, its production and use are indicative of military potential and industrial capacity.

The metal vanadium was named in 1831 by Nils G. Sefström, a chemist in the School of Mines, Stockholm, Sweden (*26*). Because some of its compounds produce solutions of beautiful colors, Sefström called the new metal vanadium, after Vanadis (surname of a race of gods in Norse mythology, to which Freya, the goddess of beauty, belongs).

Although Sefström was credited with naming vanadium, Andres Manuel del Rio, a Mexican, was the original discoverer. In 1801, when del Rio was a professor of mineralogy at the School of Mines (Colegio de Mineria) in Mexico City, he examined a sample of brown lead ore from Zimapan, Hidalgo, Mexico, and concluded that it contained a new metal similar to uranium and chromium. He named his new discovery "erythronium." Upon further study, he decided that he was mistaken and that the brown lead from Zimapan was merely a basic lead chromite containing lead oxide and chromic acid. He wrote a paper entitled, "Discovery of Chromium in the Brown Lead of Zimapan." In 1805, a French professor, Collet-Descotils, examined some of the same ore and published an article confirming del Rio's later analysis.

In 1831, Sefström, isolated del Rio's erythronium in iron ore samples from the Taberg mine in Småland and called the element vanadium. Other eminent chemists, Friedrick Wohler, J. J. Berzelius, and Sir Henry Roscoe, studied the element without finding practical uses for it. Wohler also demonstrated that it was the same element that del Rio had found earlier. Berzelius studied the chemistry of vanadium. In the 1860's Roscoe made extensive studies of vanadium and its compounds, placing it properly in the group with phosphorus (*16*). Roscoe, whose name is perpetuated by the vanadium-bearing micaceous mineral roscoelite, proved that previous workers had conducted their experiments not with the metal vanadium but with the nitride or oxide of this metal. He was the first person to isolate the silvery-white metal.

EARLY DEVELOPMENTS IN THE INDUSTRY

EXPERIMENTAL AND COMMERCIAL USES

Even with the developments in vanadium chemistry, the comparative scarcity and high cost of vanadium restricted its commercial use. In the 1860's, vanadium salts were limited to coloring agents in fabrics, leather, glass, and pottery, imparting to them various shades of blue, green, purple, or brown.

Commercial development of vanadium metal was begun as a result of metallurgical investigations by Choubley (1896), Helouis (1879), Arnold (1900), and Guillet (1904). Other scientists, such as Moissan, who in 1894 produced metallic vanadium in an electric furnace, and Gin, who made ferrovanadium aluminothermically, added to the knowledge of the properties of vanadium and its compounds.

Professor Arnold, of the University of Sheffield, England, started a chain of events about 1900, which helped to bring vanadium to its present importance. At Sheffield, England, long recognized as a world center of tool steels and fine cutlery, efforts were constantly expended to improve the products of Sheffield steel industries. Professor Arnold experimented with various alloying agents, among them vanadium, and found that additions of vanadium improved the cutting qualities of steel. His contributions, together with those of the men previously cited, resulted in armor plate with superior resistance, in tool steels with greatly improved cutting and wear-resistant properties, and in constructional steels with substantially increased useful strength without sacrificing toughness.

French scientists devoted attention to recovering vanadium from steel slags of the Schneider Works, at Creusot. The source of vanadium was the Minette iron ores of France and Luxembourg. In 1896, members of the Firming Steel Works in France experimented with armor plate, using vanadium as one of the alloying agents.

Even with all the knowledge of vanadium gained around the turn of the century, it still remained of little commercial value, because it was rare and its high cost prohibited extensive use. Shortly after the turn of the century, a series of events altered the supply situation.

DEVELOPMENT OF MINA RAGRA, PERU

Two brothers, J. J. and J. M. Flannery, had heard of the many beneficial qualities that vanadium would impart to steel when added in small quantities. They became interested in finding substantial deposits of vanadium-bearing minerals and in developing a new industry. Their search was shortened when Emilano Llona, a Peruvian, arrived in Pittsburgh in June 1905 with a sample of vanadium-bearing "coal" which he showed to the Flannery brothers. Because the vanadium oxide content of the coal ash was high, the Flannery's employed D. F. Hewett to investigate the Peruvian deposits. Before going to Peru, Hewett examined a similar material at Page, Okla. Instead of "coal," the material was asphaltite, which had intruded into faults in sandstone. Although the vanadium content was less than that of the Peruvian material, the Flannery brothers acquired a lease on the property in Oklahoma (*64*). Because of the greater size and vanadium content of the Peruvian "coal" deposits, it was decided that Hewett and a business associate, Alfred Thompson, would examine the South American deposit. In Peru, as in Oklahoma, it was apparent that they were not dealing with beds of "coal" but with lenticular bodies of asphaltite, which had been injected along a fracture parallel to the bedding of the enclosing shales and limestones. Analysis revealed that the ash content of the asphaltite varied but was uniformly lower than the ash content of most coal. According to Hewett, the vanadium content of the ash bore a constant relation to the loss on ignition (carbon, sulfur, and water) rather than the ash content.

While in Peru, Hewett met George I. Adams, a geologist employed by the U.S. Geological Survey, and Marco A. Denegri, director of the U.S. Army Corps of Engineers. A few months later (December 1905), these men brought to Hewett's attention a larger, richer vanadium deposit. They had obtained samples of another vanadium mineral from a new source. Analysis of one sample indicated 20 percent of vanadium, combined with sulfur instead of the common metals, lead, zinc, and copper.

This new mineral stimulated Hewett and Thompson's interest. Through Denegri, they met Señor Eulogio E. Fernandini, on whose property the vanadium-bearing material had been found.

On January 6, 1906, Señor Fernandini took them to his property where they met Fernandini's general manager, Antenor Rizo-Patron, and his chief engineer, Felipe de Lucio.

The next day they examined the new source of vanadium in the mountains near Quisque, which later became the noted vanadium mining area of Peru. In this area the colors of the underlying soils were shades of dark brown, brick red, orange-yellow, and olive-green. Hewett knew that these unusual colors were indicative of a large vanadium content in the surface and subsurface material.

Although only one exposure of vanadium sulfide (later called patronite in honor of Rizo-Patron who discovered the deposit) was found, the entire area was underlain by high-grade vanadium ore. Hewett was convinced that this area was the largest source of vanadium then known.

The discovery of vanadium at Mina Ragra, like that of many mineral deposits, was accidental. Rizo-Patron needed fuel for smelting. He asked the Indians to look for traces of coal in the region. Early in November 1905, an Indian brought him a specimen of black sulfide of vanadium found at Mina Ragra. In an attempt to burn the material Rizo-Patron noticed that it gave off considerable sulfur dioxide and that a brick-red ash remained. An analysis of the red ash remaining after ignition showed a high vanadium content. Rizo-Patron sent samples to Fernandini in Lima, and this was the material Hewett saw in the office of Señor Denegri.

The Flannery brothers formed the Atlas Reduction Co. in February 1906. In order that the new company might have ferrovanadium for experimental purposes, some asphaltite was burned to ash and sent to the United States. The vanadium-bearing ash was shipped to Niagara Falls, N.Y., where F. M. Beckett, of the Electro Metallurgical Co., reduced it to metal. This was probably the first time ferrovanadium was produced for experimental purposes in the United States.

In March 1906, Joseph Flannery, Alfred Thompson, and Hewett completed negotiations with Señor Fernandini for purchasing the Quisque property. The property was developed under the general supervision of Rizo-Patron and de Lucio.

Establishing a new industry in the United States required additional planning and the construction of a reduction plant. The site chosen for the plant was Bridgesville, Pa. There was also the problem of obtaining competent technical personnel to build and operate the proposed plant.

As several companies in England were making ferrovanadium from Spanish lead vanadates and several plants in France and Germany were using vanadium alloys, Alfred Thompson and James Flannery went to Europe to obtain information and competent personnel. J. Kent Smith, chief metallurgist of Willans & Robinson, Ltd., of Chester, England, agreed to design and operate the new plant. He joined the new company in December 1906.

Subsequent examination of minerals from Peru by Dr. W. F. Hillebrand, of the U.S. Geological Survey, revealed nine vanadium-bearing minerals. Six of the minerals found at Mina Ragra were new to science. Development of the mine in Peru progressed rapidly.

By the fall of 1907, the American Vanadium Co's plant for extracting vanadium was completed, and ferrovanadium became available for experimental purposes and commercial use.

The Flannerys were able to interest Henry Ford in the use of vanadium steel, and the catalog describing the 1908 Ford automobiles contained several pages on the use of vanadium steels in these cars.

In the early 1900's, other investigators became interested in vanadium alloys and compounds. Metallurgical methods were developed by B. D. Saklatwalla, who invented and successfully operated an electric furnace in which, with carbon, he reduced vanadium pentoxide to metal. Before his contributions on metallurgy, the aluminothermic method was the only commercial way to obtain ferrovanadium. Such technologic developments brought to the world steels that were especially helpful to a growing automobile industry, metal producers, and consuming industries.

CHANGING SOURCES OF SUPPLY

For many years, the Peruvian deposits were the major source of vanadium ores. Other sources were found, but only a few became commercially important.

Crude oils and some asphalts from Venezuela contained vanadium. Many ships burning Venezuelan crude oils during World War II were equipped to catch flue dust, which was treated later to recover the vanadium. During World War II, Germany obtained its supply of this vital metal from accumulations of slag resulting from the reduction of Swedish and local iron ores containing small but significant quantities of vanadium. Swedish iron ores, especially the Taberg ores, have long been known to contain vanadium.

Vanadium-bearing minerals have been found in many parts of the world, including Great Britain, Northern Rhodesia, South-West Africa, Tanganyika, Union of South Africa, Australia, Czechoslovakia, France and Luxembourg, U.S.S.R., Spain, Sweden, Argentina, Chile, Peru, and the United States. Only a few of these countries and territories, including Peru, South-West Africa, Northern Rhodesia, Union of South Africa, and the United States, have been important sources of vanadium ores. Table 24, page 70 gives production data for the worlds major vanadium producers.

Major events in the development of the vanadium industry in the United States started about 1894. About this time, certain aspects of the metallurgy, chemistry, and use of vanadium products and compounds were being ascertained, especially in Europe. In 1899 the finding of vanadium, chromium, and titanium was reported in the ash of peat from the Hyde Swamps in North Carolina (*45*).

The same year, vanadium was found in the magnetic iron ores of eastern Ontario, and uranyl vanadate deposits were discovered adjacent to the San Miguel River, San Miguel County, Colo. In 1900, roscoelite was found in Colorado in the La Plata sandstone near Placerville, San Miguel County, and in western Montrose County. Carnotite also was discovered in irregular pockets in Montrose County. The same year the ash from "coal" mined in the Province of Mendoza, Argentina, was found to contain about 10 percent vanadium. Clays and shales containing vanadium were found near Sidney, Australia, and the vanadium mineral sulvanite was recognized in southern Australia.

Vanadium oxide from France was imported into the United States for use in the dye industry in 1901. In this year, about 375 tons of vanadium-uranium ores was produced in Colorado.

In 1902, the use of vanadium in the steel industry was in an experimental stage. Tools and other equipment containing vanadium were found to be unharmed by the heat generated from cutting. Domestic vanadium production was increased in 1905 owing to demands of the newly developed automobile industry. However, it was not until 1908 that Henry Ford promoted the use of vanadium in his automobiles. Major supplies came from England.

Exploration led to the discovery in 1906 of vanadium-uranium minerals in Rio Blanco County, Colo. Another event of significance in this year was the construction of an experimental plant by the Vanadium Alloys Co. at Vanadium (formerly Newmire), 12 miles below Telluride, Colo. The following year several companies processed vanadium ore: Primos Chemical Co., Primos, Pa.; Electro Metallurgical Co., Niagara Falls, N.Y.; and American Vanadium Co., Pittsburgh, Pa., which treated ores from Peru. About this time, other vanadium-bearing materials were discovered in isolated locations in the West. Among these were lead-vanadate ores, found in Arizona in Pinal, Yavapai, and Yuma Counties and near Tucson. Other principal operations in Colorado were the plants of the Vanadium Alloys Co. and the Dolores Refining Co., at Cedar.

Continued field work in 1909 and 1910 revealed new sources of vanadium throughout the world. Vanadium-bearing minerals were discovered in Africa and Turkestan. In the United States, vanadium-bearing minerals were found in Arizona, Colorado, Nevada, New Mexico, Oklahoma, Oregon, and Utah. Some vanadinite was produced near Tucson, Ariz. This mineral also occurred near Globe, Ariz. Asphaltite near Palisade, Nev., was found to contain vanadium. In Arkansas, asphaltite having a high vanadium content was discovered at Mena. Additional asphaltite deposits were found at Page, Okla. None of the domestic occurrences and deposits of vanadium-bearing minerals outside the "four corners" area of the Colorado Plateau have since become important sources of vanadium.

Several new deposits were found in Colorado in the Paradox Valley and in the Rangely district, where carnotite was discovered. Carnotite was found also in eastern Oregon and in Utah about 10 miles from Bedrock, San Juan County.

In 1911, the use of vanadium in steel increased rapidly, causing a general decline in prices. One of the principal producers of carnotite ore in Paradox Valley, Montrose County, Colo., was the General Vanadium Co. The ore was shipped to England for processing. The same year Primos Chemical Co. treated roscoelite ore at Newmire (Vanadium), Colo.

Vanadium Mines Co., of Pittsburgh, mined deposits at Cutter, N.M., and silver-lead mine dumps were reportedly treated for vanadium at Georgetown, Grant County.

As early as 1911 there was much activity in Utah. One company, Utah Rare Metals Co., shipped ore to domestic buyers and concentrate to England.

Vanadium Corp. of America was the largest domestic producer in 1912. Primos Chemical Co. operated the plant of Vanadium Alloys Co. at Vanadium, Colo. At Placerville, Standard Chemical Co. and Curran & Hudson operated plants. Vanadium Mines Co. shipped ore from deposits of vanadium-bearing minerals from the Caballos Mountains in New Mexico. In New Mexico, deposits carrying vanadinite, molybdenum, and tungsten were discovered at Magdalena. In Pennsylvania, carnotite was discovered near Mauch Chunk.

In 1913, the principal domestic producers of vanadium ore were American Vanadium Co., Arden Wilson & Co., Colorado Carnotite Co., General Vanadium Co., McKeever & Co., Standard Chemical Co., and Primos Chemical Co.

Endlichite, a lead vanadate, was discovered near Skanee in Baraga County, Mich., in 1914. Vanadium steel production in the United States continued to rise in 1915. One of the main producers of ferrovanadium was American Vanadium Co.

In 1916, vanadium steel production was about double that of 1915. With the entry of the United States into World War I in 1917, the demand for vanadium stimulated production, especially that of ferrovanadium. Because of the increased demand, United States Vanadium Co. constructed a 50-ton mill at Kelvin, Ariz. Two other companies in Colorado also recovered vanadium. One company, Chemical Products Co., recovered vanadium from the dump of National Radium Co. The other, Primos Chemical Co., operated at Vanadium (Newmire) throughout the year.

Of significance in 1918 was the scarcity of Peruvian vanadium caused by a shortage of shipping facilities. Military requirements continued to increase consumption and brought about price increases. In Colorado the Primos chemical plant at Vanadium was destroyed by fire.

A highlight of 1919 was the selling of American Vanadium Co. to Vanadium Corp. of America. Control of vanadium production in the world passed from the Flannery family of Pittsburgh, Pa., to J. L. Replogle and Charles M. Schwab. The new owners installed an electric furnace at Bridgeville, Pa., to supplement aluminum methods. In 1919 the ferrovanadium market was stronger than in any previous year, and the use of vanadium in alloy steel was firmly established.

Although estimated carnotite reserves in Colorado increased in 1919, there was a gradual decline in carnotite production in Paradox Valley. However, activity in the Gateway district of Colorado and Utah increased. Production in Peru declined but was still about 60 percent of the world total; the balance was produced in the United States. Most of the U.S. production came from southwestern Colorado and southeastern Utah. The same year, Primos Chemical Co. rebuilt its burned mill and resumed milling in August. Colorado Vanadium Co. constructed a new mill at Sawpit to process roscoelite ore. Main producers of ferrovanadium in the United States in 1919 were: American Vanadium Co., Electro Metallurgical Co., Metal & Thermit Corp., and Standard Chemical Co.

Production of vanadium in 1920 was the largest to date. Mining of carnotite was very active. A considerable quantity of vanadium-bearing materials came from the Moab district, Utah. Also in this year, a new mill was built by David Taylor at Denver, Colo. Another event of significance was the acquisition of Primos Chemical Co. by Vanadium Corp. of America, its main competitor.

The vanadium deposit of Vanadium Corp. of America at Mina Ragra continued to be the world's largest producer of vanadium in 1921.

In 1922, Vanadium Corp. of America operated its Colorado properties; however, the Peruvian property of this company remained idle. The entire output of vanadium came from carnotite, produced as a byproduct of radium. Another event of significance was the discovery of a new deposit of carnotite and roscoelite 10 miles from Rifle, Colo.

In 1923, the only domestic producer of ore was United States Vanadium Co. A significant development in the vanadium industry in the United States in 1924 was the acquisition of two claims from Vanadium Corp. of Colo. by the United States Co. One claim was 22 miles northeast of Monticello and the other 40 miles southeast of Moab, Utah. The United States Co. reportedly built a 20-ton mill during the year.

Pittsburgh Radium Co., Denver, Colo., made iron vanadate in 1924 from ores mined at Yellow Cat Wash, about 20 miles east of Thompson, Utah. Carnotite was discovered on the west end of Vulture Mountain, near Aguila, Ariz. In Nevada, Master Alloy Mining & Milling Co. constructed a mill near Goodsprings to produce vanadinite concentrate but made no shipments.

In 1925, United States Vanadium Co. continued development of its Rifle, Colo., property. Utah Vanadium Co. and Pittsburgh Radium Co. mined carnotite on Yellow Cat Wash, east and south of Thompson, Utah.

The same year Frederick Laiste assigned to Anaconda Copper Mining Co. his patent for the separating of vanadium from phosphoric acid solutions by precipitating an alkaline earth metal with ferrocyanide.

The United States Vanadium Co. properties in Colorado were acquired by Union Carbide & Carbon Co. (now Union Carbide Nuclear Co.) in 1926, and the name was changed to United States Vanadium Corp. After the property was acquired, the mill at Rifle was enlarged to treat roscoelite. In Utah, the Utah Vanadium Co. mined ore at Yellow Cat Wash and purchased ore from the Gateway district, Long Park, Colo., and from mines in the La Salle and Carizo Mountains in Arizona. The United States Co. operated in Dry Valley, 40 miles southeast of Moab.

In 1927, two companies produced vanadium ore in the United States. United States Vanadium Corp. continued to mine and treat ore near Rifle, Colo., and to make plant improvements. From Rifle, fused vanadium oxide was shipped to Columbiana, Ohio, and to Niagara Falls, N.Y. United States Co. of New Jersey obtained claims near New Castle, in the same geological formations as the deposits of United States Vanadium Corp., and claims in the Gateway and Long Park district previously held by Radium Corp. of Colorado. The Rhodesian Broken Hill Development Co. of Rhodesia (Africa) announced a process for extracting vanadium from zinc ores. The use of vanadium alloys and chemicals continued to increase.

Except for small shipments from Nevada, the Rifle, Colo., plant of United States Vanadium Corp. was the only domestic producer of vanadium ore in 1928. United States Vanadium Corp. acquired the properties of Standard Chemical Co. in San Miguel Valley, at Long Park, and in Paradox Valley. The plant of Radium Ores Co., Denver, Colo., was sold for junk.

In 1929, more than 90 percent of world vanadium production was under American industrial control; however, only 16 percent of the total output was produced in the United States. Arizona, Colorado, and Utah continued as the center of the vanadium industry in the United States. E. C. O'Brien and Co. built a mill near Globe, Ariz., and treated vanadinite ore from the Apache

Vanadium Co. claims at Radium and Dripping Springs. A mill at Wickenburg, Ariz., was operated by United Vanadium Corp. (Los Angeles).

In Colorado, United States Vanadium Corp. acquired the Long Park holdings of Vanadium Alloys Corp. Rare Metals Corp. mortgaged its Montrose County properties to Vanadium Corp. of America, which built a mill near Naturita, Colo.

Several other properties changed hands in 1929. In Utah, Vanadium Alloys Corp. obtained the San Juan County holdings of United States Co. of New Jersey. The Dry Valley properties of Vanadium Alloys Corp. were acquired by International Vanadium Mining Corp. Several shipments of ore from Utah and Colorado were made by Western Ore Supply Co. to the Interstate-Copartner mill at Denver.

A major event of 1930 was the Tariff Act, which placed a 40-percent ad valorem import tax on vanadic acid, vanadic anhydride, vanadium salt, and vanadium chemical compounds and a 25-percent ad valorem tax on vanadium, ferroaluminum vanadium, chromium vanadium, ferromanganese vanadium, ferrosilicon vanadium, and ferrosilicon aluminum vanadium. Under the Tariff Act of 1930, ores and concentrates containing vanadium were to be admitted without import tax.

Colorado and Utah continued to supply most of the domestic production of vanadium ore in 1930; however, other areas were also important. United States Vanadium Corp. continued operations in the Rifle district of Colorado. At Dripping Springs, Ariz., United States Vanadium Corp. operated the By-Water vanadinite deposit. The International Vanadium Corp. operated its Dry Valley property southeast of Moab, Utah.

In 1931, the demand for vanadium was small. The price of vanadium ore was 26 to 28 cents per pound of V_2O_5. Other activity was confined primarily to Arizona, Colorado, New Mexico, and Utah. In Colorado, United States Vanadium Corp. continued to operate its Rifle plant. The plant of Rare Metals Corp. near Naturita was sold at auction. Some vanadinite concentrate was produced by United States Vanadium Corp. at Dripping Springs, Ariz.

In 1932 and 1933, demand for vanadium also was small, resulting in the curtailment of many operations. The Molybdenum Corp. of America acquired carnotite claims at Dry Valley from International Vanadium Corp. Kingman Refining & Smelting Corp. reportedly treated ore from Goodsprings, Nev., at its plant in Arizona.

During 1934, most of the carnotite was mined by Shattuck Chemical Co. from claims on the Dolores River in the McIntyre district, San Miguel County, Colo.

In 1935, H. W. Balsley's Yellow Circle Mining Co., Moab, Utah, produced ore in the La Sal Mountains, 16 miles from Moab, and J. W. Lewis shipped some vanadium-bearing sandstone from Grant County, Utah.

By 1935, business conditions had improved. The production of vanadium had increased but was still very small. In Arizona, Molybdenum Gold Mining Co. (subsidiary of Molybdenum Corp. of America) and Mammoth-St. Anthony recovered vanadium from complex ores containing lead, silver, and molybdenum. United States Vanadium Corp continued development at Dripping Springs, Ariz.

The carnotite-roscoelite properties and milling facilities of Shattuck Chemical Co. in western San Miguel County, Colo., were acquired by North Continent Mines, Inc., of Chicago.

Several important events occurred in 1936. Foremost among them was the rapid recovery of the vanadium industry from the depression. Production of vanadium ores was well established in the "four corners" area of the Colorado Plateau, especially in Colorado, Arizona, and Utah. During the year, International Vanadium Corp. prepared for vanadium production at Dripping Springs, Ariz. Molybdenum Corp. of America and Mammoth-St. Anthony used flotation on complex ores. United States Vanadium Corp. completed a 125-ton mill and roaster at Uravan, Colo., and started production, furnishing its own salt and coal for the process. In Utah, the Utah Vanadium Corp. mined carnotite at Cedar, Colo., and Rare Metals, Inc., operated in the Moab district.

Demand for vanadium continued to increase in 1937. Production was again derived primarily from Colorado, Utah, and Arizona. Mammoth-St. Anthony in Arizona continued operations. International Vanadium Corp. completed a 100-ton mill for Dripping Springs ore, but no vanadium was produced.

By 1938, production from Peru had decreased considerably, and the shift in source areas was noticeable. Production in the United States continued to rise. As in 1937, most of the domestic ore was produced by United States Vanadium Corp., Uravan, Colo.; however, considerable quantities were produced in Arizona and Utah (Harbro mines near Cisco), and a small amount was shipped from Goodsprings, Nev. At Gateway, Colo., Gateway Alloys, Inc., built a 20-ton mill.

Production in 1939 was about 23 percent greater than in 1938. In Arizona, the Mammoth-St. Anthony Co. acquired the mines of the Molybdenum Gold Mining Co. and added to its treatment facilities. In Colorado, United States Vanadium Corp. produced vanadium-bearing ores. The Shumway properties near Blanding, Utah, lead in production in Utah. The Harbro mines near Cisco, Utah, shipped concentrates.

In 1940, domestic production of vanadium in ores continued at about the same rate as in 1939. As in previous years, the principal producer in Arizona continued to be Mammoth-St. Anthony; however, Colorado produced most of the domestic output. United States Vanadium Corp. and Vanadium Corp. of America stimulated production by buying custom ores. United States Vanadium Corp. continued to operate its Uravan, Colo., plant at the rate of 260 tons per day. Vanadium Corp. of America reopened the Naturita, Colo., properties which had been closed since 1920. North Continent Mines, Inc., constructed a mill near Cedar, Colo.

Another significant event of 1940 was the construction of a plant at Anaconda, Mont., by Anaconda Copper Mining Co. to produce vanadium pentoxide in conjunction with its phosphate plant operations. This plant was built to produce at a reported rate of 100,000 pounds a year by recovering vanadium oxide from phosphoric acid solution.

With the entry of the United States into World War II, the year 1941 was one of planning for and starting a greatly increased domestic vanadium industry. The Government of the United States took initial steps in financing treatment plants for increased production and priority control of vanadium with the establishment of the Office of Production Management (OPM). In addition, the construction of a plant by Titanium Pigment Corp., subsidiary of National Lead Co., gave promise of adding about 1,200 tons of vanadium to domestic vanadium production. Vanadium was to be recovered as a byproduct of titanium extraction from the titaniferous magnetic deposits of the MacIntyre ore body in New York.

Operations of the United States Vanadium Corp. and Vanadium Corp. of America in Colorado were greatly increased in 1941.

In 1942, construction and preliminary work on Government-financed, but privately operated, vanadium plants was begun at Durango and Grand Junction, Colo., to be operated by United States Vanadium Corp., and at Monticello, Utah, to be operated by Vanadium Corp. of America. In mid-1942, the MacIntyre plant of Titanium Pigment Corp. was completed in New York. However, production of vanadium as a byproduct in the extraction of titanium from titaniferous magnetite ore, as originally planned by the company, did not materialize.

By early 1943, domestic production of vanadium exceeded consumption. Supplies of vanadium were not critical, even though the United States was in the midst of a war. Consequently, the Government-supported purchase program of uranium-vanadium-bearing ores was terminated on February 29, 1944. Government-owned plants at Durango, Colo., and Monticello, Utah, were shut down but left in a standby condition. In 1944, the Government mill at Durango, Colo., was sold to United States Vanadium Corp. Early in 1945, the Monticello, Utah, mill was leased by Vanadium Corp. of America from the Defense Plant Corporation.

Supplies of vanadium from domestic sources and from Peru were more than adequate from the mid-World War II years through the Korean conflict (1952). For security reasons, data on the production and consumption of vanadium-bearing ore in the United States was suspended (from 1947) at the request of the Atomic Energy Commission.

Since 1953, as well as in preceding years, the domestic vanadium mining and milling industry has been centered primarily in the "four corners" area of the Colorado Plateau. Vanadium is produced as a byproduct or coproduct of uranium mining in this area. Production of vanadium from domestic sources has exceeded demand, and the United States has become an exporter of vanadium-bearing materials. With the increased production of domestic vanadium, imports (excepting certain vanadium products) have stopped. Imports from Peru, for many years the main source of vanadium for the United States, were terminated in 1955. Unless new applications requiring large quantities of vanadium are developed, domestic supplies appear adequate for several years.

The most important source areas for vanadium ore and concentrate outside the United States have been the Broken Hill mining district of Northern Rhodesia, developed and worked by British capital; the South-West Africa deposit of Tsumeb West, originally started by German capital; the Peruvian deposits at Mina Ragra, developed and operated by American capital; and the vanadium-producing areas of the Western United States. Within the next few years, Finland may become one of the world's largest producers of vanadium from titaniferous magnetite deposits of Otanmäki. Significant production of vanadium may result from developments in the Transvaal, Union of South Africa.

CHAPTER 3. GEOCHEMISTRY AND GEOLOGY

By R. P. Fischer[5]

GEOCHEMICAL HABITS

VANADIUM IN IGNEOUS ROCKS

Vanadium is relatively abundant as a trace element in igneous rocks. It averages about 150 parts per million and is about twice as abundant as copper, 3 times as abundant as zinc, and 10 times as abundant as lead (*94*). It is more abundant in mafic rocks than in silicic ones.

Most of the vanadium in igneous rocks is in the relatively insoluble trivalent state. It is not an essential part of any common rock-forming mineral; rather its ions replace those of iron and aluminum in the common iron and ferromagnesian minerals and less abundantly in titaniferous minerals and chromite. Vanadium is relatively abundant in magmatic iron ores, especially the titanferous magnetites, where it is mainly associated with the magnetite.

VANADIUM IN HYDROTHERMAL DEPOSITS

According to Goldschmidt (*100*, pp. 490–491), the relative insolubility of the trivalent vanadium that is common in igneous rocks does not favor the introduction of this element into the hydrothermal environment. The vanadium content of most hydrothermal deposits is so low that its presence is recognized only by spectrographic analysis rather than by ordinary mineralogic study or assay. The results of Kaiser and others (*102*) on spectrographic analyses of 775 samples from representative ore deposits show an average of less than 100 parts per million (*148*), an amount notably less than the average vanadium content reported by Green (*94*) in igneous rocks (150 p.p.m. V) and shales (120 p.p.m. V). However, these 775 samples do show a tendency of vanadium to concentrate in hydrothermal vein deposits containing titanium-bearing minerals and in veins containing gold tellurides. The relative abundance of vanadium with titanium in some veins suggests that the association of these two elements in magmatic deposits extends into the hydrothermal environment. No obvious cause explains vanadium in gold-telluride veins.

VANADIUM IN THE WEATHERING CYCLE

During the weathering of igneous rocks in humid climates, much of the vanadium apparently goes into clay minerals, but it remains in the trivalent state (*78*, p. 599). If other constituents are removed by weathering, the residual material may be enriched in vanadium, as are some bauxites and lateritic iron ores. On the other hand, if the clay minerals are removed by erosion, some vanadium (perhaps a large part of it) must stay with these clay minerals as they are transported to places where they accumulate as sedimentary rocks, because argillaceous sediments are generally richer in vanadium than sandstones or limestones.

During the weathering of igneous, residual, or sedimentary rocks, some vanadium oxidizes to the quinquevalent state, especially in arid climates. In this state the vanadium goes readily into solution and remains in solution over a wide range of acidity and alkalinity. It can be precipitated from solution and locally concentrated in rocks under the following general conditions (*100*, p. 492).

1. In the presence of hydroxides of aluminum or ferric iron. This process could form or enrich the vanadium concentration in some bauxites and in some residual and sedimentary iron ores.
2. In the presence of cations of heavy metals, such as lead, zinc, and copper. This process could form the vanadate ores.
3. In a reducing environment, such as in the presence of carbonaceous material. If the vanadium-bearing solutions are moving through rocks, this process could form deposits such as those in sandstone on the Colorado Plateau. On the other hand, if the solutions are surface waters, this process could also form deposits of syngenetic metal-organic compounds and sulfides of vanadium and other metals in sediments such as carbonaceous shales which accumulate in waters depleted in oxygen. Furthermore, if the carbonaceous materials in these sedi-

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[5] Geologist, U.S. Geological Survey.

ments are converted to liquid hydrocarbons the vanadium compounds can move as dissolved constituents, and if these liquid hydrocarbons are distilled naturally to form asphaltites the contained vanadium can be residually concentrated in the asphaltite. This sequency of events could form a deposit like that at Mina Ragra, Peru.

VANADIUM IN SEDIMENTARY ROCKS

Clays and shales contain about 120 parts per million of vanadium; sandstones, about 20; and carbonate rocks, less than 10 (*94*). As a rule, vanadium content increases with an increase in argillaceous material and especially with an increase in organic matter; vanadium is rather highly concentrated in some coal, petroleum, and asphalt (*22*).

VANADIUM MINERALS AND DEPOSITS

Several dozen vanadium-bearing minerals and mineral varieties are known, but less than half of them are ore minerals. The more important vanadium source minerals are listed and described in table 11. The mineral occurrence of vanadium in many low-grade deposits is not known. Vanadium deposits are classified and described in the following section by their genetic and geochemical relations.

DEPOSITS OF MAGMATIC ORIGIN

Titaniferous Magnetite Deposits.—Vanadium is present in appreciable quantities in most titaniferous magnetites (*5*), but it occurs with the magnetite rather than the intergrown ilmenite. The V_2O_5 content ranges from about 0.2 to more than 1 percent and probably averages about 0.5 percent. Deposits of this type are associated with both gabbros and anorthosites, but the largest and most promising deposits economically are those associated with anorthosites. Some bodies of titaniferous magnetite are merely local differentiates of the magma, and the concentrated masses of the metallic minerals merge with the nonmetallic minerals of the host rock and contain disseminated crystals of the rock minerals. In some igneous complexes, such as the Bushveld in Africa, extensive stratiform sheets of titaniferous magnetite are present (*50*). Some bodies have been injected into the host rock, presumably after the ore minerals remelted in the place where they originally crystallized; such bodies have well-defined borders, and many are nearly pure mixtures of ilmenite and magnetite. Titaniferous magnetite deposits vary greatly in size, but many of them are large and contain millions of tons of ore.

Representative deposits of this type are those at Lake Sanford, N.Y., which have been described by Balsley (*48*) and Stephenson (*55*), and the deposit at Iron Mountain, Wyo., described by Diemer (*39*) and by Newhouse and Hagner (*81*).

Nontitaniferous Magnetite Deposits.—Vanadium is reported in some magmatic magnetite deposits that are so low in titanium (0.1 to 1.0 percent TiO_2) as to be classified as nontitaniferous. Most magnetites of this type are derivatives of syenitic magmas; some bodies have differentiated in place, whereas others have characteristics that indicate pegmatitic or hydrothermal transport.

Vanadium is reported in only a few of the deposits, and these contain 0.1 to about 0.3 percent V_2O_5. It is not known whether vanadium is negligible in other deposits of this type or has not been detected. The phosphorus content is usually high in such deposits.

The deposits in the highlands of northern New Jersey contain only about 1.0 percent TiO_2 and probably belong to the nontitaniferous class. According to analyses published by Bayley (*3*), the vanadium content of these ores ranges from 0.08 to 0.21 percent V_2O_5. The large magnetite deposit at Kiruna, Sweden, contains 0.14 to 0.20 percent V_2O_5 (*1*) and appears to belong to this class, as does the nearby deposit at Gällivare.

VANADIUM-BEARING HYDROTHERMAL VEINS

Vanadium is sparse in typical hydrothermal veins except ones containing titanium minerals and gold.

Nolanite, a new iron-vanadium mineral, has been found in some uranium-bearing veins in the Goldfields district, Saskatchewan, Canada (*112*). The mineral is black, has a bladed habit, and has the approximate composition of $4FeO{\cdot}V_2O_3{\cdot}4V_2O_4$ (*132*). It is described as intergrown with ilmenite and other vein minerals.

Vanadium is associated with davidite (a U-Ti-Fe mineral) at Radium Hill, Australia (*103*), and in the Mt. Isa-Cloncurry district, Australia (*130*). The average vanadium content of these ores is not reported.

Samples from the titanium deposits of rutile and brookite at Magnet Cove and Potash Sulphur Springs, Ark., show different amounts of vanadium, but the average vanadium content of these deposits is only a few tenths of 1 percent V_2O_5 (*99*).

The association of roscoelite, the vanadium-bearing mica, with gold-quartz veins, especially those containing gold-telluride minerals, was noted many years ago (*4*). Commonly, the roscoelite is finely intergrown with quartz and other gangue minerals, and in places it forms small aggregates along the vein walls. Eckel (*69*, p. 61) states that roscoelite-bearing quartz, which is green, is an almost certain indication of high-grade gold-telluride ore in the La Plata district, Colo. Lovering and Goddard (*76*) mention the presence of roscoelite in numerous veins in several mining districts in the

TABLE 11.—*Principal ore minerals of vanadium*

Class	Name	Composition	Color	Habit	Association	Principal occurrences as ore minerals
Sulfide	Patronite	VS_4 or V_2S_5	Greenish black.	Massive, with conchoidal fracture.	With quisqueite, a hydrocarbon (asphaltite).	Mina Ragra, Peru.
Oxide	Montroseite	$VO(OH)$ or $(V,Fe)O(OH)$.	Black	Bladed crystals and aggregates.	With vanadium silicates.	Colorado Plateau, U.S.A.
Silicate	Roscoelite	$(Al, V)_2(AlSi_3)(K,Na)O_{10}(OH,F)_2$.	Greenish, gray brown.	Micaceous	With V and U minerals in pores in sandstone. In gold and gold-telluride veins.	Do. Colorado and California, U. S. A.; Australia.
	V-bearing chlorite.[1]					Colorado Plateau, U.S.A.
	V-bearing hydromica.[2]					Do.
Vanadate.	Vanadinite	$Pb_5(VO_4)_3Cl$	Red to brown and yellow.	Prismatic crystals and fibrous crusts.	In vanadate ores, with base metals.	South-West Africa, Northern Rhodesia, Southwestern United States, Mexico, and Argentina.
	Descloizite	$Pb(Zn,Cu)VO_4(OH)$	Red to brown and black.	Crystalline and fibrous, in radial aggregates.	do	Northern Rhodesia, South-West Africa, Mexico, Southwestern United States, and Argentina.
	Mottramite	$Pb(Cu,Zn)VO_4(OH)$	Black	Finely crystalline crusts.	do	South-West Africa, Southwestern United States.
	Carnotite	$K_2(UO_2)_2(VO_4)_2\cdot 1\text{–}3H_2O$.	Yellow	Powdery or finely crystalline.	With other V and U minerals in pores in sandstone and as replacements of fossil wood.	Colorado Plateau, U.S.A.; widely distributed elsewhere, but rarely abundant.
	Tyuyamunite	$Ca(UO_2)_2(VO_4)_2\cdot 7\text{–}10\frac{1}{2}H_2O$.	Yellow to greenish.	do	With other V and U minerals in pores and fractures in limy rocks.	Tyuya Muyan, Russia; Colorado Plateau, U.S.A.
	Metatyuyamunite.[3]	$Ca(UO_2)_2(VO_4)_2\cdot 5\text{–}7H_2O$.				Do.
	Corvusite	$V_2O_4.6V_2O_5\cdot nH_2O$.	Blue black.	Aggregates replacing and cementing sandstone.	With other V minerals.	Colorado Plateau, U.S.A.

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[1] Much like roscoelite in all respects, but a chlorite instead of a mica.
[2] Essentially the same as roscoelite.
[3] Essentially the same as tyuyamunite.

Colorado Front Range; all are classed as gold-telluride veins except one, which is classed as pyritic gold. Roscoelite also occurs with gold-telluride ore at Cripple Creek, Colo., and Kalgoorlie, Australia, and with gold-quartz veins in California and Oregon, some of which contain gold-telluride ore.

RESIDUAL DEPOSITS ACCUMULATED BY WEATHERING

Small to moderate quantities of vanadium are concentrated in bauxite and aluminous and ferruginous laterites and related soils, especially those derived from the weathering of basic igneous rocks. Goldschmidt (*100*, p. 492) says that the vanadium in lateritic bauxite may amount to several thousand parts per million. Fox (*9*, p. 205) reports 0.55 percent V_2O_5 in ferruginous laterite at Coolgardie, Australia. Judging from an incomplete review of the voluminous literature on bauxites, however, it appears that most bauxites do not contain more than 0.10 percent V_2O_5; Jost (*22*) reports an average content of 600 parts per million of vanadium (0.11 percent V_2O_5).

DEPOSITS OF SEDIMENTARY ORIGIN

Deposits in which vanadium accumulated with the sedimentary host rock consist of chemical precipitates, such as sedimentary iron ores; mechanical sediments, such as shales; and strata rich in organic materials, such as coal. These deposits form slowly under relatively uniform conditions. Although the vanadium content of most of these deposits is small, their grade usually is quite constant, and many of them are extensive and contain enormous tonnages.

Iron Ores.—Vanadium is not reported in many published analyses of sedimentary iron ores; however, its omission from an analysis does not necessarily indicate its absence, as it has been found in nearly all types of sedimentary iron ores. Most extensive deposits of sedimentary iron are rather low in vanadium, but they do form large potential sources of vanadium. According to Hallimond (*13*) the important Jurassic iron ores of the Cleveland Hills district, England, contain 0.08 percent V_2O_3 (nearly 0.10 percent V_2O_5). The highly productive "minette" ores of Lorraine and the Salzgitter ores of Germany contain 0.02 to 0.20 percent V_2O_5; these ores yielded much vanadium during World War II (*59, 150*).

Phosphates of Southeastern Idaho.—Although most marine phosphates contain very little vanadium, those in southeastern Idaho contain from a few hundredths to a few tenths of 1 percent V_2O_5. The phosphate rock is in one or more layers in the phosphatic shale member of the Phosphoria formation and its stratigraphic equivalents. These rocks extend over an area of about 100,000 square miles in the adjoining parts of Idaho, Montana, Wyoming, Utah, and Nevada, but only the phosphate rock in Idaho is known to contain much vanadium. Besides vanadium, the phosphate rock also contains fluorine and a little uranium and selenium. Not all of the minerals containing these elements have been identified; however, it is believed that these elements were precipitated from sea water with the phosphate rock, as their content in a single bed is nearly constant.

Vanadiferous Shales.—In addition to the vanadium-bearing phosphate rock in the phosphatic shale member of the Phosphoria formation in southeastern Idaho, some shale beds in this stratigraphic unit in the adjoining parts of Idaho and Wyoming contain appreciable quantities of vanadium. Individual shale beds are thin, ranging from a fraction of an inch to several inches in thickness, but they are extensive and have a nearly constant vanadium content. The greatest concentration is in a zone ranging from about 2 to 10 feet thick, about 35 to 50 feet below the top of the phosphatic shale member. Beds in the central few inches of this zone contain as much as 1.5 to 2.5 percent V_2O_5, and the entire zone averages about 0.85 percent V_2O_5. These beds also contain 0.02 to 0.1 percent molybdenum, 0.02 to 0.3 percent nickel, and as much as 0.1 percent selenium. The minerals containing these elements have not been identified. Similar vanadiferous shales are present in the Camp Floyd district, Tooele County, Utah.

Perhaps the vanadium-bearing shales of Peru, which are reported to average more than 1 percent V_2O_5 for a thickness of 30 feet (*12*), are also of this type. Swedish oil (alum) shales of Cambrian age also contain a few tenths of 1 percent V_2O_5 (*37*).

Other Sedimentary Deposits.—Vanadium- and titanium-bearing magnetite sands, presumably derived from titaniferous magnetite deposits, are reported in many parts of the world. Some are stream deposits, but most are beach sands. Those in New Zealand (*54*) may be of special interest because of their extent and the possibility of their supporting a local iron industry.

Although most coals seem to be nearly devoid of vanadium, some contain appreciable amounts. Analyses showing several percent of vanadium in coal ash are not uncommon.

EPIGENETIC DEPOSITS FROM SOLUTIONS OF OBSCURE ORIGIN

DEPOSITS WITH URANIUM IN SANDSTONE AND LIMESTONE

Colorado Plateau.—The vanadium-uranium deposits of the Colorado Plateau form a group of widely distributed deposits with many common characteristics. Although these deposits are found in many formations, ranging in age from late Paleozoic to middle Tertiary, the more productive deposits are restricted to a few stratigraphic units of Mesozoic age. Most of the deposits are in sandstone beds of continental origin, although some are in brackish-water limestone and a few are in fresh-water shale. The host rocks in nearly all deposits contain carbonaceous material, mostly fossil wood; asphaltic material is closely associated with some deposits, and residual petroleum is also found in or near a few deposits.

The early minerals in the ore consist of low-valent oxides and silicates of vanadium and uranium, small amounts of copper and iron sulfides, and traces of galena and sphalerite. The ore minerals alter to higher valent oxides of vanadium and to vanadates and other secondary uranium minerals. They mainly occupy pore spaces in the sandstone, although in part they replace sand grains and associated argillaceous and carbonaceous material. The ore bodies are tabular layers that lie nearly parallel to the bedding but do not follow the beds in detail. Most ore bodies are small, but they range from masses only a few feet across to ones several hundred feet across. The average content of ores yielding vanadium is about 1.5 percent V_2O_5.

It is generally thought that the ore minerals were introduced into their present positions by solutions, but the nature of these solutions and the source of the metals are not known. Some investigators believe that the solutions were hypogene and that the metals were introduced from deep-seated sources; others favor the idea that the metals were originally disseminated in the ore-bearing and associated rocks and were transported and concentrated at favorable sites by aqueous solutions or possibly petroleum. It is also generally thought that sedimentary structures, such as lenses, influenced the migration of the ore-bearing solutions and the localization of many ore deposits. In addition, the regional distribution of deposits suggests to some geologists that regional deformation influenced localization by providing pathways for the vertical movement of solutions to ore-bearing beds. A few deposits show a close association with such vertical pathways. Igneous activity and mineralization of definite hydrothermal origin are not closely associated with vanadium-uranium deposits, except in a few places.

McKelvey, Everhart, and Garrels (*110*) list most references to reports on these deposits.

Other deposits in the United States.—Deposits having geologic characteristics similar to those on the Colorado Plateau have been found in most Western States and in Pennsylvania and New Jersey. They occur in rocks of Paleozoic, Mesozoic, and Cenozoic ages. None of these deposits contains enough vanadium to make recovery of this metal profitable under present conditions. Of the known deposits, those in the Black Hills of South Dakota and Wyoming contain the most vanadium (about 0.2 to 0.5 percent V_2O_5). More information on these deposits is contained in a report by Finch (*121*) and the references cited by him.

Tyuya Muyan, U.S.S.R.—At Tyuya Muyan, Fergana, in central Asia, oxidized uranium, vanadium, and copper minerals are associated with barite, calcite, and quartz in limestone. The ore bodies are pipelike structures that partly fill cavities and perhaps partly replace the host rock. The area has a complex structure and geologic history, with considerable faulting and igneous activity.

Pavlenko (24) ascribes the origin of these deposits to thermal solutions derived from diabase intrusives. On the other hand, Fersman (*17*), according to Bain (*74*, p. 295), considers that the uranium and vanadium were leached from nearby black shales. According to Rankama and Sahama (*78*, p. 638), these shales contain approximately 400 grams per ton of uranium and 850 grams per ton of vanadium. The ore has been mined for radium and uranium; possibly some vanadium has been produced as a byproduct.

VANADATE ORES WITH BASE METALS

Vanadates of lead, zinc, and copper are found in many base-metal deposits in the Southwestern United States, Mexico, South America, Spain, Africa, and Australia. Vanadium has been produced from a number of these deposits; the most productive have been those in the Otavi district, South-West Africa, and at Broken Hill, Northern Rhodesia. Most, although not all, of these deposits are in carbonate country rock. Typically, they are in areas of moderately arid climate and deep oxidation; the vanadate ores are in the oxidized parts of the deposits.

Evidence and opinions differ as to the source of the vanadium in these deposits. Skerl (*25*) reports that the unoxidized ore at Broken Hill was tested chemically and spectrographically, but no trace of vanadium was found. Clark (*18*) states that the primary ores in South-West Africa contain little or no vanadium and believes that no reasonable amount of concentration from the weathering of eroded lead-zinc ore bodies could account for the vanadium ore; Verwoerd (*134*) obtained similar evidence and arrived at the same conclusion as Clark. In both areas the vanadium is thought to have come from that originally disseminated in the surrounding rock. The same explanation has been offered for other deposits.

In contrast to the evidence and opinions mentioned, Peterson (*29*) finds that the vanadate minerals at the Mammoth-St. Anthony area, Ariz., were introduced during the last stage of hypogene mineralization and later than the base-metal sulfides.

Otavi District, South-West Africa.—The mines near Otavi and Tsumeb, South-West Africa, are in replacement bodies in limestone and dolomite. The primary ore minerals are pyrite, bornite, sphalerite, enargite, tetrahedrite, galena, and chalcocite. Vanadium ore minerals occur in the oxidized zones of these deposits and consist of descloizite, mottramite, and vanadinite.

Broken Hill, Northern Rhodesia.—The deposits in the Broken Hill district, Northern Rhodesia, consist of descloizite and vanadinite bodies associated with and marginal to oxidized lead-zinc replacement masses in dolomite.

Southwestern United States and Mexico.—Vanadate minerals are reported in the oxidized zones of more than 400 base-metal deposits in the Southwestern United States (*8*); however, vanadium ore has been produced only from the Mammoth area, Pinal County, Ariz., the Goodsprings district, Nev., and a few other areas. Similar deposits occur in Mexico, and a few of them have also been productive.

In the Mammoth area most of the country rock is granite, probably of Precambrian age. The ore occurs as fissure filling along two fractures, the Collins and Mammoth-Mohawk veins. According to John Wood, mine superintendent, the average per-ton yield of oxidized ore was about $4.00 in gold, 5 pounds of MoO_3, 2 pounds of V_2O_5, and a little silver and lead; some zinc and copper also are present in this ore. Wood reported that the content of gold, molybdenum, and vanadium decreases sharply below the zone of oxidation and that the unoxidized ore consists of lead, zinc, and copper sulfides.

In the Mammoth-Mohawk vein, Peterson (*29*, pp. 47, 55) reports that oxidation shows no decrease to the 750-foot level, which is a short distance below the present water table, and that the amounts of vanadium and molybdenum increase with depth. In the Collins vein, on the other hand, vanadium and molybdenum minerals decrease in quantity below the 520-foot level and are virtually non-existent on the 700-foot level, whereas lead and zinc increase below the 520-foot level and form massive sulfide bodies on the 700-foot level.

The Collins and Mammoth-Mohawk veins are separated by the postmineral Mammoth fault, which probably cuts the Mammoth-Mohawk vein at a depth of about 900 feet (*29*, section C–C′, p. 2). This fault and the oxidation relations have caused some investigators to believe that the Mammoth-Mohawk vein is a down-faulted segment of the Collins vein. A displacement of 1,200 feet would be required. Peterson (*29*, p. 25) believes that the displacement is only 150 to 200 feet.

In these veins the vanadium minerals are vanadinite, descloizite, and mottramite; molybdenum occurs in the mineral wulfenite ($PbMoO_4$). Although these minerals occur only in the oxidized ore, where they form crystals and crusts on the leached material of the veins, Peterson (*29*, p. 47) attributes this leaching to hydrothermal solutions and believes that the vanadium and molybdenum minerals were introduced in the last stage of hydrothermal action.

In the Goodsprings district the vanadate minerals form thin coatings on fragments of dolomite breccia and on fossil corals in the oxidized parts of the lead-zinc deposits (*98*, p. 66).

VANADIUM-BEARING HYDROCARBONS

Asphaltic Deposits of Peru.—Peru has yielded about 50 million pounds of vanadium, which is about one-fourth of the world's total recorded production. Nearly all of the Peruvian vanadium has come from the asphaltic deposit at Mina Ragra, the world's most productive deposit. This deposit was found in 1905 (*2*).

Unoxidized ore consists of quisqueite (a hydrocarbon), coke, and patronite (vanadium sulfide); several vanadates formed in the zone of oxidation. Bravoite, a nickel-iron sulfide, is present in small amounts with the patronite.

Country rock at Mina Ragra comprises shales and thin-bedded limestone of Cretaceous age. These rocks are invaded by several igneous dikes and cut by numerous faults near the deposit. The ore minerals and associated material occupy a fracture and permeate the adjoining shale, forming a lens-shaped body at least 50 feet wide and several hundred feet long at the surface; the body apparently bottoms at a depth of about 250 feet (*88, 128*).

Although the origin of this unique deposit has not been clearly determined, most authorities (*2, 22, 128*) relate its formation to the process responsible for forming asphaltite and its common contamination by vanadium. Thermal solutions, however, may have played a part in transporting or altering the asphaltite and enriching this deposit.

Similar vanadiferous asphaltic veins are common in this part of Peru; all are apparently in the same group of sedimentary beds, which also contain vanadiferous black shales. Although none of these asphaltic veins is nearly as rich in vanadium as the Mina Ragra deposit, they do contain about 1 percent vanadic oxide (*2, 6, 128*).

Other Asphaltic Deposits.—Numerous references to vanadium in asphaltite and related substances are cited in the literature, especially by Clarke (*10,* p. 723), Rankama and Sahama (*78,* pp. 594–603), and Goldschmidt (*100,* pp. 485–499). The ash is said to contain up to about 40 percent vanadium. Occurrences that appear worthy of special attention as potential sources are reported in Argentina, Mexico, Venezuela, Russia, and the United States.

Petroleum Ash and Refinery Residues.—Some crude oils contain as much as a few percent of vanadium (*11, 129*) in the ash. Certain petroleums from Venezuela and Mexico are relatively rich in vanadium, whereas others contain little or none. The differences between vanadium-bearing and barren oils has not been established, and it is not known whether the vanadium accumulated with the oil in the source bed or was derived from the rocks through which the oil may have migrated.

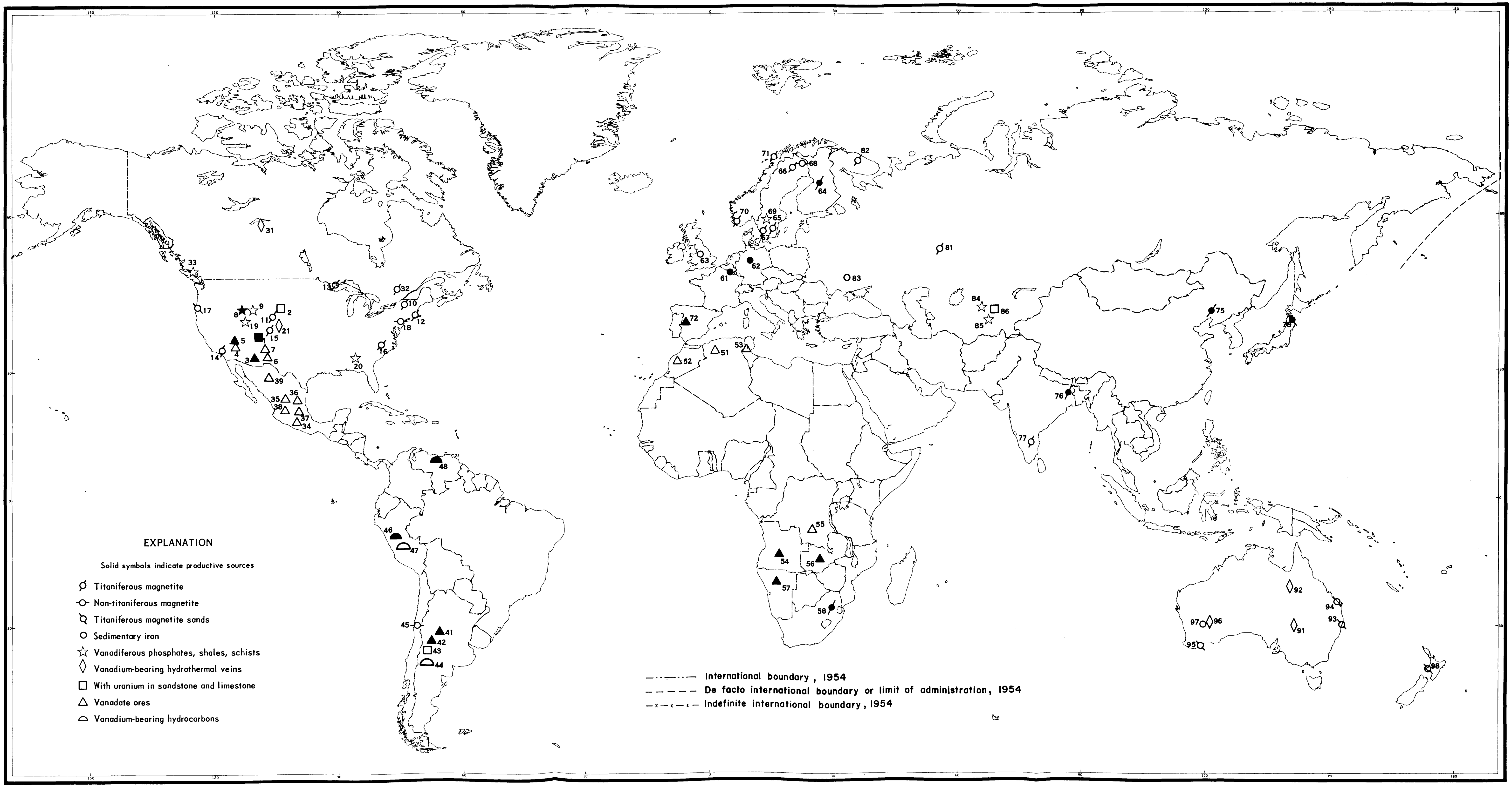

FIGURE 2.—World's Important Productive and Potential Sources of Vanadium, Classified by Types
(Courtesy U.S. Geological Survey)

CHAPTER 4. RESOURCES

By R. P. Fischer[6]

INTRODUCTION

The total world resource of vanadium is very large, but few known deposits are rich enough in vanadium to be worked profitably for this metal alone. Only one deposit—the vanadium-bearing titaniferous magnetite in Transvaal, Union of South Africa—has a large enough reserve to furnish a substantial share of world requirements. Nevertheless, since the late 1940's the annual production of vanadium has equaled or exceeded demand. Some sources yield vanadium only as a byproduct of such low value that the geology, grade, and even reserves of vanadium had little or no influence in selecting the site and scope of operations.

World resources of vanadium are itemized in table 12. Where sampling and development appear adequate to express the total quantity of vanadium in deposits or where calculations of reserves are available, figures are given (table 12, column 4). Where the tonnage or grade information of known deposits is scant or where it is geologically reasonable to assume that new deposits can be found by exploration, vanadium resources are expressed in qualitative terms (table 12, column 5). These deposits and even some of smaller or undetermined significance are described in the text.

The world's important productive or potential sources of vanadium are shown by deposits or localities in figure 1. These same sources are classified as productive or potential and by geologic types in figure 2.

NORTH AMERICA

UNITED STATES

Colorado Plateau Deposits.—Deposits near Rifle, Placerville, and Rico, Colo. (*62, 119*) are so low in uranium that they have been mined solely or mainly for vanadium (fig. 3). Although ore production from these deposits has been small in recent years the deposits have nearly one-half million tons of developed ore reserves, which range from 1.5 to 2.0 percent V_2O_5 and contain nearly 10 million pounds of vanadium. Undiscovered or potential resources, largely in the Placerville district, may total several million tons of rock averaging 1.5 to 2.0 percent V_2O_5.

Most of the deposits that have yielded significant quantities of both vanadium and uranium (fig. 3) are in southwestern Colorado, southeastern Utah, and northeastern Arizona (*44, 84*). Virtually the entire vanadium output in the last 5 years has come from these deposits. In 1957 known reserves, classed as available for mining, totaled about 4,350,000 tons of ore averaging about 1.64 percent V_2O_5 and containing nearly 80 million pounds of vanadium (Production Evaluation Division, Grand Junction Operations Office, U.S. Atomic Energy Commission). This reserve is adequate to sustain operations at the 1958 rate for only a few years. Although material of this general grade in the ground probably amounts to several times the known reserve and constitutes a very large resource, it will be increasingly costly to find and develop. Consequently, the production of this type of ore may decrease in a few years as the Atomic Energy Commission (AEC) contract support for vanadium is reduced.

Northwestern New Mexico, eastern and central Utah, and northeastern Arizona (fig. 3) contain the largest reserves of uranium ore and are yielding most of the uranium ore produced in the Colorado Plateau region. This ore contains as much as 0.5 percent V_2O_5 and averages about 0.13 percent V_2O_5. Known deposits contain about 75 million pounds of vanadium (Production Evaulation Division, Grand Junction Operations Office, AEC); this reserve, plus the vanadium in undiscovered deposits, represents a very large resource. At present, no effort is being made to recover vanadium at mills treating this ore. However, the rated capacity of the mills in operation and those being built is so large that the tailings produced annually will contain more than half as much vanadium as is now used.

Other Deposits of the Colorado Plateau Type.—Uranium deposits similar to those on the Colorado Plateau have been found in other parts of the United States; a few are in Eastern States, but the majority are in the western part of the country (*121*). Most

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[6] Geologist, U.S. Geological Survey.

TABLE 12.—*Estimated total resources of vanadium*

Map localities (figs. 1 and 2)	Country and locality or type	Approximate content of V_2O_5, percent	Vanadium contained: Estimates or calculations in known deposits, million pounds V	Vanadium contained: Additional potential resources [1]
	North America:			
	United States:			
1	Colorado Plateau, vanadium ores	1.75	10	Large.
	Colorado Plateau, uranium-vanadium ores	1.64	80	Very large.
	Colorado Plateau, uranium ores (low V)	.13	75	Do.
2	Black Hills, S. Dak. and Wyo.	.25	.9	Moderate.
3	Mammoth, Ariz.	[2] 1.0		Small.
4	San Bernardino County, Calif.	[2] 1.0		Do.
5	Goodsprings, Nev.	[3] 1.0		Do.
6	Cutter, N. Mex.	[2] 1.0		Do.
7	Magdalena, N. Mex.	[2] 1.0		Do.
8	Phosphate deposits, Idaho	.2–.3		Large.
9	Vanadiferous shales, Idaho and Wyo.	.8–.9	600	Very large.
10	Lake Sanford, N.Y.	.45	600	Do.
11	Iron Mountain, Wyo.	.4		Large.
12	Iron Mine Hill, R.I.	.3		Do.
13	Duluth gabbro deposits, Minn.	[2] 1.0		Very large.
14	Los Angeles Co., Calif.	[2] .3		Moderate.
15	Colorado, Caribou and Iron Mountain	[2] .3		Do.
16	Western North Carolina	(4)		Do.[2]
17	Curry County, Oreg.	[2] .7		Small.
18	New Jersey deposits	.1–.2		Moderate.
19	Camp Floyd district, Utah	.5–1.0		Small.
20	Alabama flake graphite	(4)		Moderate.
21	Colorado Front Range	[2] 2.0		Do.[2]
	Canada:			
31	Goldfields area, Saskatchewan	(4)		Small.[2]
32	Provinces of Quebec and Ontario	[2] .5		Very large.
33	Quadra Island, British Columbia	(4)		Small.
	Mexico:			
34	State of Guerrero	(4)		Do.[2]
35	State of Zacatecas	(4)		Do.[2]
36	State of San Luis Potosi	(4)		Do.[2]
37	State of Hidalgo	(4)		Do.[2]
38	State of Guanajuato	(4)		Do.[2]
39	State of Chihuahua	(4)		Do.[2]
	South America:			
	Argentina:			
41	Province of Cordoba	(4)		Do.[2]
42	Province of San Luis	(4)		Do.[2]
43	Province of Mendoza	(4)		Do.[2]
44	Province of Neuquen and Mendoza	(4)		Do.[2]
45	Chile, Tofo	.25		(4)
	Peru:			
46	Mina Ragra	3.0	.33	Small.[2]
47	Other vanadiferous asphaltites and shales	1.0		(4)
48	Venezuela, petroleum	(4)		Large.[2]
	Africa:			
51	Algeria	(4)		Small.[2]
52	French Morocco	(4)		Do.[2]
53	Tunisia	(4)		Do.[2]
54	Angola	(4)		Do.[2]
55	Belgian Congo	(4)		Do.[2]
56	Northern Rhodesia	(4)		Moderate.[2]
57	Southwest Africa	(4)		Do.[2]
58	Union of South Africa	(4)		Very large.[2]
	Europe and Asia:			
	Central European countries:			
61	"Minette" ores of France, Luxembourg, Belgium, and Germany.	.02–.2		Large.
62	Salzgitter ore of Germany	.02–.2		Do.
63	England, Cleveland Hills	.1		Do.[2]
64	Finland, Otanmaki	.5	250	Very large.
	Sweden:			
65	Taberg	[2].4		Do.

TABLE 12.—*Estimated total resources of vanadium*—Continued

Map localities (figs. 1 and 2)	Country and locality or type	Approximate content of V_2O_5, percent	Vanadium contained	
			Estimates or calculations in known deposits, million pounds V	Additional potential resources [1]
66	Ruoutevare	.26		Large.
67	Kramsta	.4		Very large.
68	Kiruna	.1–.2		Do.
69	Alum Shales	[2].2		Large.
	Norway:			
70	Ekersund area	(4)		Very large.[2]
71	Lofoten Islands	(4)		Large.[2]
72	Spain, Santa Marta	(4)		Small.[2]
75	China, Jehol Province, Manchuria	[2].5		Moderate.
76	India, Bihar	[2]1.7		Large.
77	India, Mysore	(4)		Do.[2]
78	Japan, Hachinohe	.42		Do.
	U.S.S.R.:			
81	Ural Mountains	[2].5		Very large.
82	Kola Peninsula	(4)		Large.[2]
83	Kersch, Ukraine	1.6		Do.
84	Kara Tan Mountains	(4)		Do.[2]
85	Alai Mountains	(4)		Do.[2]
86	Tyuya Muyan	(4)		Moderate.[2]
	Oceania:			
	Australia:			
91	Radium Hill, South Australia	(4)		Small.[2]
92	Mt. Isa-Cloncurry, Queensland	(4)		Do.[2]
93	Ti-Fe deposits and sands, New South Wales	(4)		Large.[2]
94	Ti-Fe sands, Queensland	(4)		Do.[2]
95	Ti-Fe deposits, Western Australia	(4)		Do.[2]
96	Kalgoorlie, Western Australia	(4)		Small.[2]
97	Coolgardie, Western Australia	(4)		Large.[2]
98	New Zealand, North Island	.3–.5		Very large.

[1] "Small"—less than 1 million pounds V; "Moderate"—1 to 10 million pounds V; "Large"—10 to 100 million pounds V; "Very large"—more than 100 million pounds V.

[2] Questionable.

[3] 4,304 tons of vanadate "ore" purchased by Metals Reserve Company during World War II, mostly from Goodsprings, averaged 0.98 percent V_2O_5.

[4] Unknown.

of these deposits contain little or no vanadium, but those in the Black Hills of South Dakota and Wyoming contain 0.2 to 0.5 percent V_2O_5. Known uranium ore reserves in this area contain nearly 900,000 pounds of vanadium (Production Evaulation Division, Grand Junction Operations Office, AEC), and total resources are probably a few times larger.

The widespread distribution of deposits of this general type in the United States, some of which contain significant quantities of vanadium, permits optimism that other similar vanadium deposits may be found.

Vanadate Deposits.—Although vanadate minerals are reported in numerous base-metal deposits in the Southwestern United States, their vanadium yield has amounted to less than 1 percent of total world production. Nearly all of the domestic production of vanadate has come from the Mammoth area in Arizona, where vanadate production was begun in 1934 and discontinued in 1944. A little ore has come from Goodsprings, Nev., and perhaps from a few other localities. Although deposits in other districts, the more promising of which are shown in figures 1 and 2, might yield a small production at times, no significant domestic production of vanadate ore can be expected. No figures are available on reserves, but the potential of all districts is thought to be small.

Phosphate Deposits.—Byproduct vanadium was recovered from 1941 to 1954 from phosphate rock mined at Conda, Idaho. The total represented about 1 percent of the world vanadium output. The rock mined contained about 0.29 percent V_2O_5 (*71*). Although a figure is not available for minable reserves of phosphate rock at Conda, phosphate-bearing beds containing 0.2 to 0.3 percent V_2O_5 are thought to be extensive, so the total reserve probably is large. A small yield of byproduct vanadium might be expected under favorable conditions in the future from Conda or other phosphate rock mines in southeastern Idaho.

Vanadiferous Shale Deposits.—The Phosphoria formation in the adjoining parts of Idaho and Wyoming contains vanadiferous shale beds in addition to vanadium-bearing phosphate rock. Beds richest in vanadium are in a zone a few feet thick near the middle of the formation, but as these beds are not adjacent to the phosphate layers they could not be mined as a unit with the phosphate rock. No vanadium has been produced commercially from these shales, but they do represent a very large potential source of this metal. Sampling in several areas has shown the vanadiferous zone to contain 0.7 to 1.25 percent V_2O_5 or an average of about 0.85 percent throughout the region. Indicated resources, calculated for a minimum mining thickness of 3 feet, total about 65 million tons of rock above drainage levels. The vanadium contained in this material, roughly 600 million pounds, is about three times greater than the total world production of vanadium before 1958. Inferred resources are many times larger according to V. E. McKelvey in a letter to the author.

Titaniferous Magnetite Deposits.—Although vanadium-bearing magnetic concentrates from titaniferous magnetite deposits have been used as iron ore in Europe and some vanadium has been recovered from this source, not much material of this type has been used in blast furnaces in the United States. Where used, however, it has been blended with nontitaniferous iron ore to reduce the titanium content, presumably below the point of profitable extraction of the vanadium.

The vanadium-bearing titaniferous magnetite deposits of Lake Sanford, N.Y., are being mined principally for titanium. The ore is a coarse-grained intergrowth of magnetite and ilmenite in anorthosite and gabbro. According to Lawthers (*131*, p. 39), the ore averages 34 percent iron and 18 to 20 percent TiO_2, and known reserves in the area total 121 million tons of ore, of which about 100 million tons is available. From various sources of information, it is estimated that the ore averages about 0.45 percent V_2O_5; thus, the total reserves contain about 600 million pounds vanadium. The magnetic concentrate from the ore averages 56 percent iron, 9 to 10 percent TiO_2 (*131*, p. 39), and about 0.7 percent V_2O_5 (*48*).

Although no vanadium is being recovered from the Lake Sanford ore at present, 1 million tons of this ore, which is about the current annual rate of production, contains about 5 million pounds of vanadium, which nearly equals the world's annual rate of vanadium consumption in recent years.

Only a very general appraisal can be made of the many other titaniferous magnetite deposits in the United States. In the following paragraphs most of the figures on tonnage and on iron and titanium grade are taken from Lawthers (*131*, pp. 36–42). Specific credit is given to the original source of the vanadium-grade figures.

The deposits at Iron Mountain, Wyo., are lenses and tabular bodies of titaniferous magnetite in anorthosite. The titaniferous magnetite consists of finely intergrown ilmenite and magnetite containing about 0.4 percent V_2O_5 (*39*). Estimates of reserves range from 9 million to 178 million tons.

The deposit of Iron Mine Hill, R.I., is estimated to contain about 7 million tons of material assaying about 33 percent iron, 10 percent TiO_2, and 0.3 percent V_2O_5. Although these figures indicate a large amount of vanadium in the deposit, the ilmenite and magnetite are too finely intergrown to separate economically.

The Duluth gabbro in Minnesota contains many deposits of titaniferous magnetite. Although these deposits total about 90 million tons of material, they are not considered an economic source of iron or titanium, as the high-grade ore bodies are too small and the large ore bodies are too low grade. However, published assays show an unusually high vanadium content, reaching 2.6 percent V_2O_5 and perhaps averaging 1 percent or more (*5*). If the higher grade assays are representative of individual deposits, it might be feasible some day to treat this material primarily for vanadium, as is being done with titaniferous magnetite ore in the Union of South Africa. (See p. 39.) Whether economic or not, the ore bodies in the Duluth gabbro constitute a very large potential source of vanadium.

There are many deposits of titaniferous magnetite in Los Angeles County, Calif.; a few are beach and stream placers, but most are in place in anorthosite and gabbro. Some have been explored, and a few have been worked on a small scale for titanium concentrate. Estimates of ore reserves range from a few hundred thousand tons to several million tons, but because the ilmenite and magnetite are finely intergrown the deposits have not been intensively developed. Published assay results showing vanadium con-

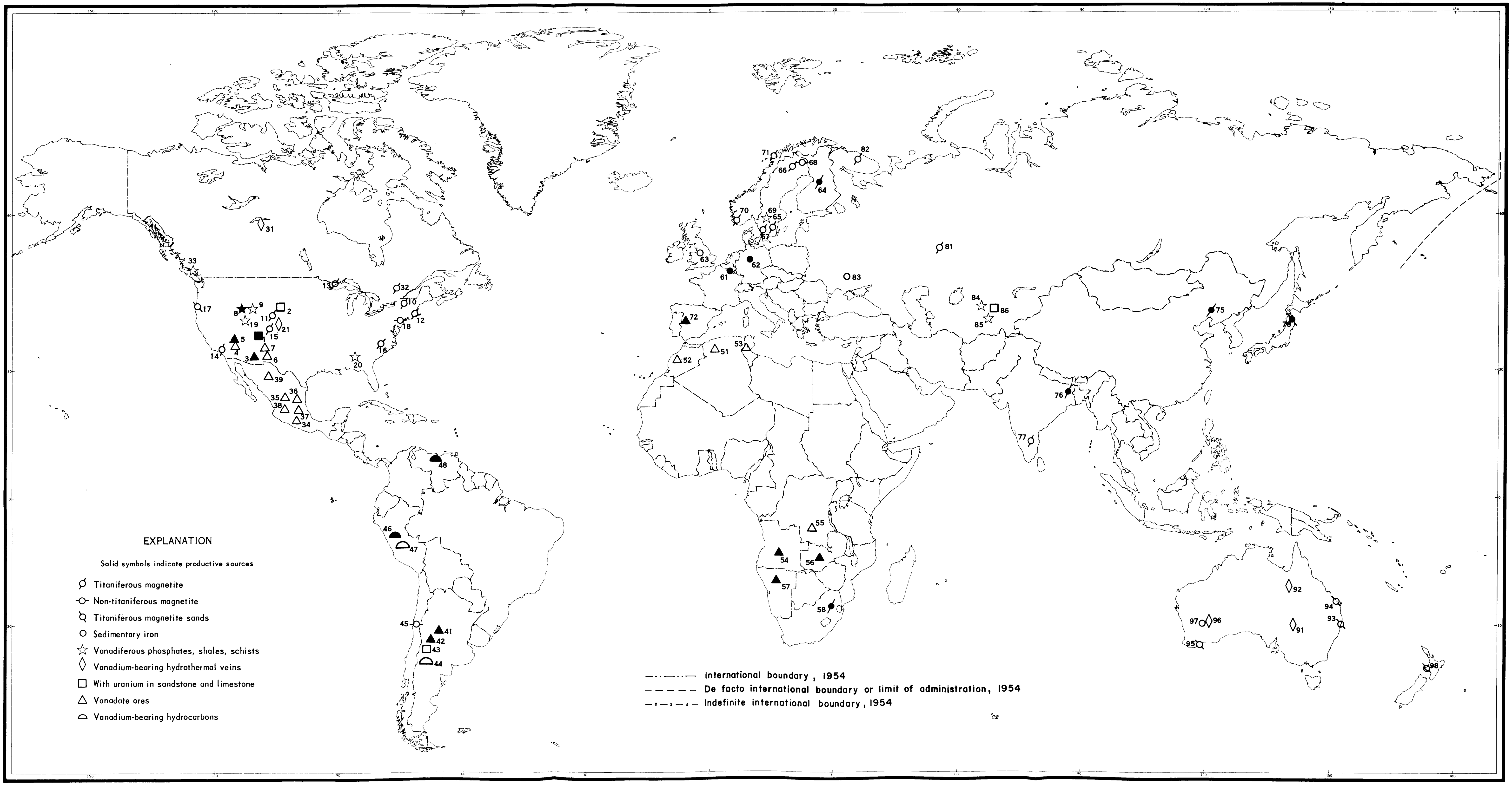

FIGURE 2.—World's Important Productive and Potential Sources of Vanadium, Classified by Types
(Courtesy U.S. Geological Survey)

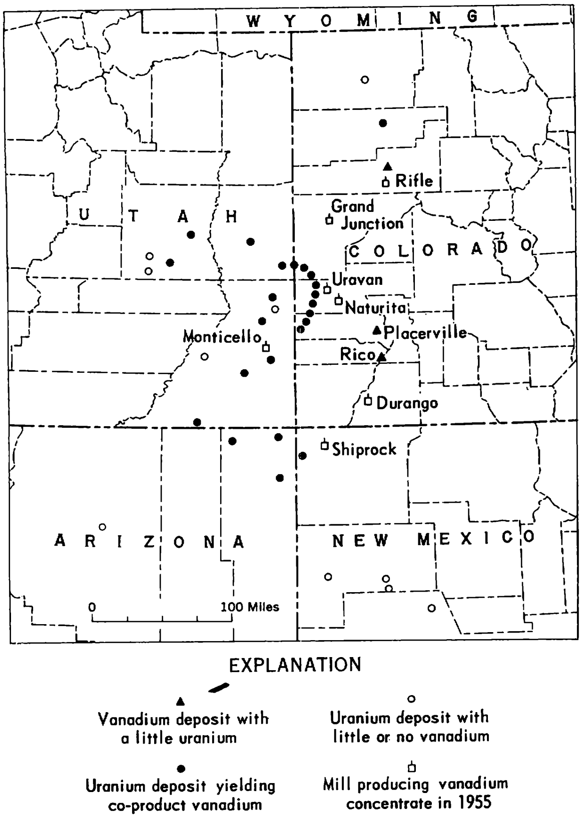

FIGURE 3.—Index Map of Adjoining Parts of Colorado, Utah, Arizona, and New Mexico, Showing Principal Areas of Vanadium and Uranium Mining and the 7 Mills That Produced Vanadium Concentrate in 1955.

tent are few but indicate a probable average grade of a few tenths percent V_2O_5 in deposits in place, making a resource of at least moderate size.

Numerous magnetite deposits in western North Carolina contain ilmenite or rutile. Published assay reports (*7, 5*) show a considerable range in titanium and vanadium content; however, some of the more titaniferous deposits appear to be unusually low in vanadium.

A small potential resource is the vanadium-bearing blacksand deposit in Curry County, Oreg. (*53*). This deposit contains about 55 percent iron, 0.4 percent vanadium, and 2.7 percent TiO_2. The deposit is lenticular, a few hundred feet long, 100 feet wide, and 35 feet in maximum thickness; it contains a few hundred thousand tons of black sand.

Magnetite Deposits.—Several magnetite deposits in New Jersey have been mined on a moderate scale. These deposits are generally classed as nontitaniferous, as their titanium content averages only about 1.0 percent TiO_2. Published assays of the ore (*3*) show 0.08 to 0.21 percent V_2O_5. Although this vanadium content is probably much too low for profitable extraction under ordinary conditions, it is about the same as that in the iron ores from which the Germans recovered vanadium during World War II; hence, these deposits can be considered a potential resource, although one of only moderate size.

Resources of Small Potential.—A small deposit of vanadiferous shale, similar to the vanadium-bearing shales of Idaho and Wyoming, has been found in the Camp Floyd district, Tooele County, Utah.

Flake-graphite deposits of Alabama have been worked in times of emergency. These deposits contain a vanadium-bearing green mica that offers a moderate potential source of vanadium.

The presence of roscoelite, the vanadium-bearing mica, in numerous veins in several mining districts in the Colorado Front Range has been mentioned by Lovering and Goddard (*76*). All deposits are classed as gold-telluride veins except one, which is classed as a pyritic gold vein. No figures of tonnage and grade of vanadium-bearing rock are given except for the Kekionga-Magnolia vein, Magnolia district, which is described (*76*, p. 234) as follows:

> It is well known for the unusual variety of tellurides. * * * Vanadium is associated with the ore, and in 1910 some ore was shipped for its vanadium content * * * some of the ore contained as much as 6.28 percent of vanadium oxide, and a moderate tonnage averaging 2 percent vanadium oxide was blocked out. The ore with a marked vanadium content extended for a distance of 1,500 feet along the surface and to a depth of 400 feet. The average of a large number of tests, including a sample taken from a carload of 20 tons, was 4.3 percent vanadium oxide.

These deposits represent a vanadium resource of at least small potential.

The ashes of some natural asphaltites in Oklahoma, Arkansas, Nevada, and elsewhere in the United States contain appreciable quantities of vanadium and are potential sources of the metal, although probably they have small significance.

A small quantity of vanadium is recovered in the United States from the treatment of chromite ores for the chemical industry.

CANADA

No production of vanadium has been recorded in Canada. Some uranium-bearing veins in the Goldfields area, Saskatchewan, offer a potential supply (*112*, p. 68). No figures on reserves are available.

Titaniferous magnetites are numerous in the Provinces of Quebec and Ontario. Many deposits are high in titanium and iron, some are large, and several have been mined. Not many published analyses of the ores give vanadium content, but those that do indicate that about one-half percent V_2O_5 is common.

A small deposit of vanadium-bearing shale is reported on Quadra Island, British Columbia (*21*).

MEXICO

Vanadate minerals have been reported in the oxidized parts of base-metal deposits in the following States of Mexico: Guerrero, Zacatecas, San Luis Potosi, Hidalgo, Guanajuato, and Chihuahua. Vanadium ores have been mined from at least some of these deposits, but information on the exact sources of these ores is not available.

Some Mexican crude oils contain a little more than average quantities of vanadium. The soot or refinery residue products of these oils might be a potential or actual source of a little vanadium.

SOUTH AMERICA

ARGENTINA

A small production of vanadium from Argentina has been reported since 1939. The output has been credited mainly to vanadate ores, but some of this vanadium may have been obtained from the ash of asphaltite or coal. No information is available regarding reserves, but continued small production from either the vanadate or the carbonaceous deposits may be expected.

The vanadate ores are in the oxidized parts of base-metal deposits in the Provinces of San Luis and Cordoba.

Sandstone deposits containing uranium and vanadium, somewhat similar to deposits on the Colorado Plateau in the United States, are reported in the Province of Mendoza (*122*, p. 75–81). However, the reported vanadium content (0.1 to 0.2 percent) is so low that these deposits are of questionable value as a vanadium resource.

In the Provinces of Mendoza and Neuquen the ash of some carbonaceous material variously described as asphaltite or coal is notably rich in vanadium; samples containing nearly 40 percent V_2O_5 have been reported (*10*, p. 723).

CHILE

The magnetite ores from Tofo, Chile, contain about 0.25 percent V_2O_5. Although no vanadium is known to have been recovered from these ores, extraction processes were investigated during World War II. Information regarding reserves is not available.

Vanadate minerals occur with base-metal deposits in several places in Chile, but no production from these sources has been reported.

PERU

The asphaltic vein at Mina Ragra (*2, 88, 128*) has been the world's most productive single deposit of vanadium. It has yielded about 50 million pounds of vanadium in ores and concentrates, representing about one-fourth of the total world production. Mining was stopped in 1955, and the mine and mill (owned by Vanadium Corp. of America) were placed on a standby basis. According to McKinstry (*128*), who reviewed the report by Aquije (*128*): "All that is left now of this fabulous deposit is a hole 850×380 feet in area and 210 feet deep with a remnant of a vein which, according to the author (Aquije), does not exceed 10,000 tons of 1.75 percent V content."

The shale country rock adjacent to the ore body, which is reported to be weakly mineralized with vanadium, might be a potential resource.

Similar vanadiferous asphaltic veins are common in this part of Peru, and all are apparently in the group of sedimentary beds that also contains vanadiferous black shales. Although none of these asphaltic veins is known to be as rich in vanadium as the Mina Ragra deposit, they do contain about 1 percent V_2O_5 (*2, 6*). When prices for vanadium have been good, small quantities of this asphaltite have been burned, and vanadium-bearing ash containing as much as 20 percent V_2O_5 has been shipped (*47*). These deposits offer a potential source, but not enough information is available to make a quantitative appraisal.

Hess (*12*) reports vanadiferous shales as much as 30 feet thick with an average content of more than 1 percent V_2O_5 in Peru.

VENEZUELA

Some Venezuelan crude oils contain more vanadium than is commonly present in petroleum, and the flue dust and ashes from furnaces burning this oil have long been sources of small quantities of vanadium. Residue products from some refineries also were treated for vanadium during World War II. These oils probably represent a resource of potential significance, but a quantitative analysis cannot be made.

AFRICA

NORTH AFRICAN COUNTRIES

Vanadate minerals of unknown potential occur with some base metal deposits in Algeria, French Morocco, and Tunisia.

CENTRAL AND SOUTH AFRICAN COUNTRIES

Angola.—A production of 11 short tons of vanadium in ores and concentrates is credited to Angola in 1956. No information regarding the source of this vanadium is available; however, it is probably vanadate ore.

Belgian Congo.—The following is quoted from the American Consul's dispatch, Elizabethville, Belgian Congo, July 18, 1956, page 17:

> Although the Mines Service reports the production of 844 tons of zinc-vanadium ore, it gives no information on grade or value. This is a new production and is apparently from the Kossu region of Bas Congo. The 1956 report of the Ramoco Syndicate, active in this area, states that underground work has been started for the development of the deposit discovered in 1954. It seems possible that this has not yet been marketed and for that reason no value was assigned by the Service.

Northern Rhodesia.—Base-metal deposits in the Broken Hill district, Northern Rhodesia (*25*) have yielded nearly 11 million pounds of vanadium in vanadate ores and concentrates. Data are not available on reserves of vanadium ore.

South-West Africa.—Production of vanadate ores from mines near Otavi and Tsumeb, South-West Africa (*18, 23*) began in 1920 and since 1925 has been quite steady at a yearly rate of nearly a million pounds of vanadium in ores and concentrates. In recent years, the entire output has come from mines of the South West Africa Co., Ltd., near Otavi. No data regarding vanadium ore reserves are available.

Transvaal.—The stratiform sheets of vanadium-bearing titaniferous magnetite in the Bushveld complex, Transvaal, have long been considered a potential source of vanadium (*35, 50*). These deposits became an actual source in 1957, when ore was produced for treatment at a newly constructed mill at Witbank, owned and operated by Minerals Engineering Co. (Ltd.), S. A. The weathered rock at the outcrop is being mined in open cuts. This material contains about 1.6 percent V_2O_5 and is being treated with a salt roast to extract the vanadium. Expected recovery is about 2 million pounds of vanadium a year.

An estimate of 50 million pounds of recoverable V_2O_5 (28 million pounds of vanadium) has been published (*136*).

A large deposit of titaniferous magnetite is reported in central Natal, and large deposits of heavy beach sands are reported along the southeast coast of Africa (*131*), but no information on the vanadium content of these deposits is available.

EUROPE

CENTRAL EUROPEAN COUNTRIES

The minette or Lorraine iron ores of the adjoining parts of France, Luxembourg, Belgium, and Germany and the Salzgitter iron ores of central Germany contain 0.02 to 0.20 percent V_2O_5. These deposits are of sedimentary origin. The ore reserve is very large.

Because Germany was critically short of other ferroalloys in World War II, the German iron industry was forced to recover vanadium from these ores. Extraction in 1943 and in 1944 totaled about 6 million pounds (*59*), which was about twice the U.S. production in 1943, the most productive war year. Resumption of the German wartime blast-furnace practice would again yield much vanadium, as iron ores from the same deposits are still being used in the central European iron industry. A small yield of byproduct vanadium was also obtained from Swedish and Norwegian iron ores treated in Germany. Small quantities of byproduct vanadium from the treatment of bauxite ores are occasionally credited to Germany and France.

No deposits rich enough in vanadium to be mined for this metal alone are known in central Europe.

ENGLAND

The sedimentary iron ores of the Cleveland Hills district, England, contain about 0.10 percent V_2O_5. The total reserve of iron is probably large.

SCANDINAVIAN COUNTRIES

Many deposits of vanadium-bearing iron ore, mostly of the titaniferous type, occur in Finland, Norway, and Sweden (fig. 2, p. 36). These deposits offer a large potential source of vanadium.

Magnetic concentrates from a deposit of titaniferous magnetite at Otanmäki, Finland, contain about 1 percent V_2O_5. The Otanmäki Company, owned by the Finnish Government, began mining in 1954. Reserves are estimated at 50 million tons of ore (*87*), which contain approximately 250 million pounds of vanadium.

Other deposits of titaniferous magnetite occur in Finland (*131*), but information on their size and vanadium content is not available.

Table 13 summarizes pertinent information on some of the vanadium-bearing iron deposits in Sweden.

TABLE 13.—*Reserves of vanadium-bearing iron deposits in Sweden*

Name	Reserves, short tons	Grade, percent [1] [2]			Remarks
		V_2O_5	TiO_2	Fe	
Taberg........	[3] 165,345	0.23-0.62	4-10	38-41	Fine Ti-Fe intergrowths.
Ruoutevare....	[3] 33,069	.26	11.1	52.1	Remote location.
Kramsta......	[3] 27,557	.40	3-5	24	Numerous deposits.
Ulvön.........	[3] 22,046	(?)	8	53	Do.
Kiruna........	[4] 1,075,000	.14-.20	.05	70	Large production.

[1] von Seth, 1925 (*14*).
[2] Zieler, 1938 (*30*).
[3] Magnusson, 1950 (*77*).
[4] Stutzer, 1906 (*1*).

The alum (oil) shales of southern Sweden are extensive and contain as much as a few tenths percent V_2O_5 (*37*). These shales offer a large potential source of vanadium, especially if vanadium could be obtained as a byproduct of rock treated for uranium and oil.

Very large deposits of titaniferous magnetite occur in the Ekersund area, Norway; some are being worked for titanium. Large deposits are also present on the Lofoten Islands and in the adjoining area, and similar deposits occur in other places in Norway. Vanadium is said to be present in the Norwegian deposits, but specific information on the vanadium content is not available.

SPAIN

Base-metal deposits with vanadate minerals near Santa Marta in the Province of Badajos, Spain, are reported to have yielded a small production of vanadium many years ago and perhaps recently, but no accurate record of production or information on reserves is available.

U.S.S.R.

Although there are no figures of Russian vanadium production, actual or expected production is frequently reported in trade journals. Soviet geologists and geochemists have studied the occurrence and distribution of vanadium rather intensively. Their results, recorded in Russian literature, are not readily available.

Titaniferous magnetite deposits are numerous in the Ural Mountains, and some have many millions of tons of "ore" (*131*); Zieler (*30*) reports vanadium contents up to 0.7 percent (1.25 percent V_2O_5). Titaniferous magnetites are also numerous on the Kola Peninsula. The large residual iron deposits at Kersch, Ukraine, contain 0.08 to 0.10 percent vanadium (0.14 to 0.18 percent V_2O_5) (*30*). Turkestan has deposits of vanadium-bearing phosphate rock in the Kara Tan Mountains, vanadiferous shales or schists in the Alai Mountains, and uranium-vanadium deposits in the Tyuya Muyan area; the first two are low-grade but large deposits, and the last is probably of higher grade but might not contain as much vanadium as the others. Some vanadium may also have been recovered from the ash of petroleum products and coal, especially in the Ural region.

ASIA

CHINA

Titaniferous magnetite deposits in the Jehol Province, Manchuria, were worked during the Japanese occupation of World War II. Reserves total about 2 million tons and are estimated to contain 55 percent iron, 14 percent titanium, and 0.3 percent vanadium.

INDIA

Vanadium ore has been reported from Dublabera, Bihar, India, but no figures are given of actual vanadium output. The ore averages about 0.96 percent vanadium (1.7 percent V_2O_5). One analysis reports 2.36 percent V_2O_5, 14.20 percent TiO_2, and about 48 percent iron. The vanadium-bearing titaniferous magnetite deposits in this area have been described by Dunn and Dey (*28*), who report 1,120,000 tons of ore reserves. If all this material averages 1.7 percent V_2O_5, more than 20 million pounds of vanadium is present.

Still larger deposits of titaniferous magnetite in Mysore are reported by Radhakrishna (*82*), but no information is available on their vanadium contents.

Some of the largest resources of titaniferous beach sands in the World occur in India (*131*). Information on their vanadium content is not available, but some vanadium is known to be present. Its possible extraction from titanium pigment liquors was considered during World War II.

The ash of lignite deposits in Travancore contains 2 percent V_2O_5, and green mica in schists in the Bhanadara district is reported to contain 0.48 percent V_2O_3 (0.58 percent V_2O_5) (*60*).

JAPAN

Many millions of tons of titaniferous magnetite beach sands are available in Japan; the sampled material averages 0.24 percent vanadium (about 0.42 percent V_2O_5). No other sources of vanadium are known in Japan.

OCEANIA

AUSTRALIA

A small quantity of byproduct vanadium might be recoverable (or may actually have been recovered) from the treatment of titaniferous uranium ore at Radium Hill, South Australia, and in the Mt. Isa-Cloncurry district, Queensland. Black, titaniferous sand deposits are common in Australia, especially in New South Wales and Queensland, and primary titaniferous magnetite deposits occur in New South Wales and Western Australia; some vanadium might be recoverable from these deposits. In addition, vanadate minerals occur with base-metal deposits in various places; the vanadium-bearing mica roscoelite is associated with gold-telluride veins in Kalgoorlie, Western Australia; and vanadium-bearing ferruginous laterites occur at Coolgardie, Western Australia. Information is not available to appraise quantitatively the resources of these occurrences.

NEW ZEALAND

Deposits of black sand totaling several hundred million tons of material occur along the west coast of North Island, and smaller deposits occur at places on South Island. The opaque minerals in some of the North Island deposits contain 8 to 10 percent TiO_2, 53 to 60 percent Fe, and 0.3 to 0.5 percent V_2O_5 (*85*). Experiments in the extraction of vanadium directly from the concentrates are in progress (*111*).

CHAPTER 5. TECHNOLOGY

PROSPECTING AND EXPLORATION

Before portable field radiometric instruments were developed, prospecting for uranium-vanadium bearing minerals was confined largely to examining outcrops. The color and appearance of certain uranium-vanadium minerals served as guides to deposits of economic importance. The development of field radiation-detection devices made prospecting much easier. Radiometric instruments enable the prospector to detect radioactive minerals in rocks that give little visible indication of their presence (*105*, pp. 9–18). Two types are commonly used—the Geiger counter and the scintillation counter. The latter is very sensitive and frequently is used in airborne or vehicle surveys. Geiger counters are less expensive and are satisfactory for surface prospecting for uranium minerals sometimes associated with vanadium.

Exploration of uranium-vanadium deposits is done by conventional methods. Excavating surface trenches and pits by pick and shovel, blasting, or mechanized equipment are convenient and inexpensive methods for determining the extent of mineralized outcrops. For mineralized horizons that do not outcrop, exploratory work usually consists of drilling with churn, rotary, or core drilling rigs. Where there are surface indications of an ore deposit, drilling is also used to ascertain the depth of an ore body.

Drilling on a 50- to 200-foot grid pattern has been the customary practice for delineating the size, depth, and physical characteristics of subsurface ore bodies. Diamond-drilling equipment has been used extensively on the Colorado Plateau. The cores or cuttings provide geologic information on the size, attitude, and physical and chemical nature of the mineralized horizons.

MINING

With the advent of nuclear weapons and nuclear energy, which require large quantities of uranium, the uranium-vanadium mining industry has grown rapidly. Since 1948, when small operators hauled ore from entryways in hand buckets, many changes have taken place in mining methods and types of ore retrieved.

Before 1948, uranium-vanadium mines were simple operations. Small lenses or pod-like mineralized bodies near the surface were developed through adits or inclined entries. Deposits were worked by a few men using hand tools, and mining was highly selective. Some operators still use similar mining methods; however, owing to the increased demand for uranium, large low-grade deposits now contribute most of the ore produced. These large deposits require more complex mining methods than small lenses or pods. Vertical shafts more than 600 feet deep are needed in some mines of the Colorado Plateau.

Although shaft mines predominate, there is a large open-pit mine in the Grants area of New Mexico, and numerous smaller surface mines are scattered on the Colorado Plateau and in Wyoming.

UNDERGROUND MINING

Many earlier Colorado Plateau uranium-vanadium deposits were discovered and developed at mineralized outcrops along rim exposures of mesas and buttes. Beds were usually mined by a system of horizontal, or nearly horizontal, workings developed from their rims by adits (*105*, pp. 19–32). Although some of the later discoveries found by drilling beyond the earlier discovered rim exposures were also developed by adits, those more distant from rim outcrops require shafts to retrieve the ore.

Stoping.—Open stoping is the principal underground mining method on the Colorado Plateau (*105*, pp. 32–38). In some mines, rock bolts are used for side and roof support. Openings may be unsupported if the ore body is narrow and elongated. If ore is uniformly distributed within a strata, room-and-pillar-mining is usually done. Irregular ore bodies may permit random spacing of waste pillars. Upon reaching the limits of an ore body, ore pillars may be extracted by controlled caving on the retreat.

Haulage.—Three types of underground haulage are used for uranium-vanadium mining on the Colorado Plateau (*105*, pp. 38–50). The length of haul and irregularity of ore occurrence dictate the selection of the tramming method. In irregular deposits and in some small mines, ore is transported by wheelbarrow or by hand in ore cars. Other small mines developed by adits use animal haulage. In larger mines, track or trackless mechanical haulage is used.

Compressed-air and electric-battery locomotives are used underground on the Plateau. Trolley-type electric locomotives are less suitable. Mine cars are loaded chiefly with compressed-air overthrow loaders.

Large diesel haulage units are used in some mines developed by adits or inclined entries. Dump trucks with capacities of 20 tons or more are used if the grade does not exceed 15°. Mines using trackless haulage may also be equipped with large-capacity scrapers and tractor-loaders, either of front-end or overhead dump design.

In many mines, small, self-propelled, three-wheel dump cars are used for tramming ore or for secondary haulage.

SURFACE MINING

The vanadium content of Colorado Plateau uranium deposits mined by surface mining methods is small, and probably very little vanadium is retrieved from such ore. However, vanadium may be recovered from open-pit mine ores in the future.

Ore from uranium-vanadium mines of the Colorado Plateau is usually transported by truck from mine to mill or stockpile. The haul from mine to mill sometimes exceeds 200 miles but usually is less than 100 miles.

TYPICAL MINING OPERATIONS

Vanadium Corp. of America.—This producer of vanadium ore has mines in several Western States (*149*).

The Monument No. 2 mine is in Monument Valley, which extends from San Juan County, Colo., into northern Apache and Navajo Counties, Ariz.

The uranium-vanadium ore bodies are localized in conglomeratic sandstone stream channels of two types—a long type, traceable for more than 2 miles, and a short type, less than 2 miles long. The channels range in width from 50 to over 2,000 feet. Channel floors are undulatory and extremely irregular, as evidenced by workings in the Monument No. 2 mine. Channel sediments contain abundant fossil wood, and in the Monument No. 2 mine the quantity of mineralized wood is high. Ore is not continuous along a channel's length or restricted to any particular sector. At the Monument No. 2 mine, ore was found in lower, middle and upper beds of channel sediments and along channel flanks. Some major ore bodies occur as flattened cylindrical bodies referred to as logs or trees by the miners.

Exploratory openings are driven into the uranium-vanadium formation from the outcrop (fig. 4 and fig. 21, p. 76). Ore deposits vary in width, making it difficult to lay out mining operations in advance.

Initially, conventional seam mining was used. As mining continued, seam mining was modified to strip mining to lower costs. The overburden was loosened with explosives and removed by bulldozers and highlift tractors. The ore was loaded into trucks and transported to the crushing and concentrating facilities. Surface mining was less selective than underground mining.

Union Carbide Nuclear Co.—The company operates mines in several districts throughout the Colorado Plateau. Many of the properties date back to radium-vanadium activities of the early 1900's.

Lense-shaped sandstone ore bodies in the Sphinx and St. Patrick mines of the Uravan Mining district have been mined sporadically since 1911. Near the mines, the beds strike N. 50° W. and dip 6° to 8° NE. The ore bodies have an irregular but pronounced dip to the southeast. Three overlapping ore lenses are present, with 6 to 18 feet of barren rock between lower, middle, and upper ore layers. The thickness of lenses in these two mines ranges from 3½ to 7 feet. Mudstones associated with the sandstones are mineralized with uranium and are of shipping grade.

Entry to the Sphinx mine is through a 105-foot-long, 6- by 7-foot, 28° incline. Stopes on an upper split of the ore zone intersect the incline 70 feet from its collar. The St. Patrick mine is entered through a short adit near the Sphinx incline. Haulageways in old sections of both mines were often irregular and small and were driven in the direction in which the ore bodies extended. Inclines followed the vertical deviation of the ore. Newer drifts are 5 by 7 feet in section and, where possible, are advanced on grades that permitted hand tramming. (See fig. 5.)

As is the common practice on the plateau, airleg-mounted drills and ⅞-inch hexagonal drill steel are used. Drill steel 5 feet long is used, also 1 ⅝-inch, four-wing, one-use-type bits, which are hand surfaced to increase drilling life.

The rock is easy to drill and break. An average of 16 holes loaded with 30-percent semigelatin dynamite usually will break 5

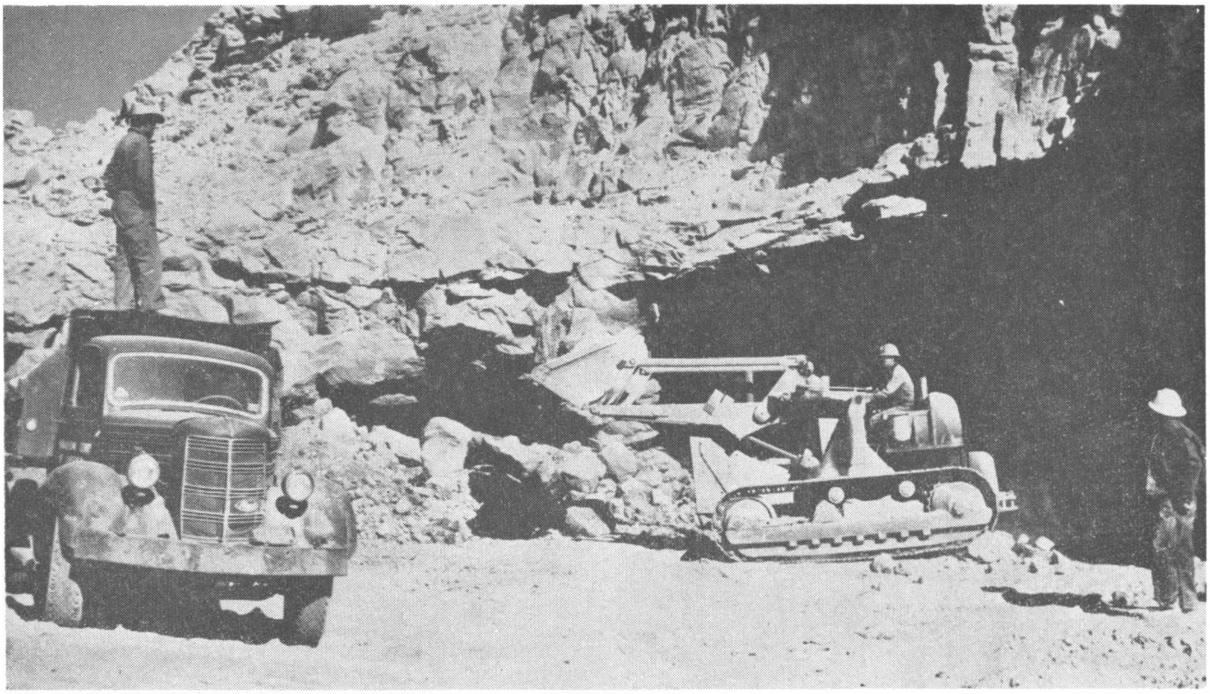

FIGURE 4.—A Tractor-Loader Scraping Up and Loading Vanadium-Uranium-Bearing Ore at the Vanadium Corp. of America's Monument No. 2 Mine, Monument Valley, Utah.

feet of ground in a 5- by 7-foot heading. If the ground is fractured, as few as 12 holes may be required. Drillers use sectional steel with the leg-mounted machines to drill 18-foot exploration holes.

Occasional stulls are used in stopes where there are large fractures. When it is certain that all ore has been mined, the stopes are backfilled.

Ore is hand trammed in 20-cubic-foot cars over 18-inch-gage rails. Single 5-horsepower air hoists are used to haul the cars to the surface. Wheelbarrows and timber slides are used to move broken ore from stopes benched above track level. When loading mine cars by hand, rough sorting is done to maintain ore grade. Ore fines are gathered with heavy mortar hoes.

At a Union Carbide Nuclear Co. mine near Rifle, Colo. (*20*), a room-and-pillar mining method is used. The deposits are lenticular assemblages of sandstone, with impure limestone and clay (fig. 6). The overlying sandstone forms a strong roof over the mine workings, thus eliminating the need for many supports. Figure 7 shows the method used in developing this mine.

Utex Exploraiton Co.—The mine of the Utex Exploration Co. (*97*) is about 39 miles southeast of Moab, Utah. Exploration by diamond drilling and subsequent mining operations after a shaft had been constructed gave information on the nature and extent of the ore body.

Development was done for a modified room-and-pillar system with 50- and 100-foot intervals. Headings were driven 12 to 15 feet high, because the ore ranged in thickness from 10 to 23 feet. Drift headings measured approximately 12 by 12 feet in cross section. Ore was broken by drilling and blasting, loaded with tractor loaders, and transported to surface stockpiles in diesel-powered tandem trucks equipped with exhaust scrubbers to cut down air contamination. Dozer-shovel end loaders were used to load ore from stockpiles into trucks for transport to ore-buying stations and mills.

The timbered mine shaft served as a manway and pipeway and for transportation of supplies. Virtually no other timber supports were used in the mine. Rock bolting was used in backs of drifts and other locations.

The inclined adit, shaft, and raises driven to the surface provided some natural ventilation, but mechanical ventilation was also used.

The Anaconda Co. (*139*).—The Jackpile mine of The Anaconda Co. is on the Laguna Indian Reservation, Valencia County, N. Mex., about 45 miles west of Albuquerque. Although the Jackpile is operated only as a

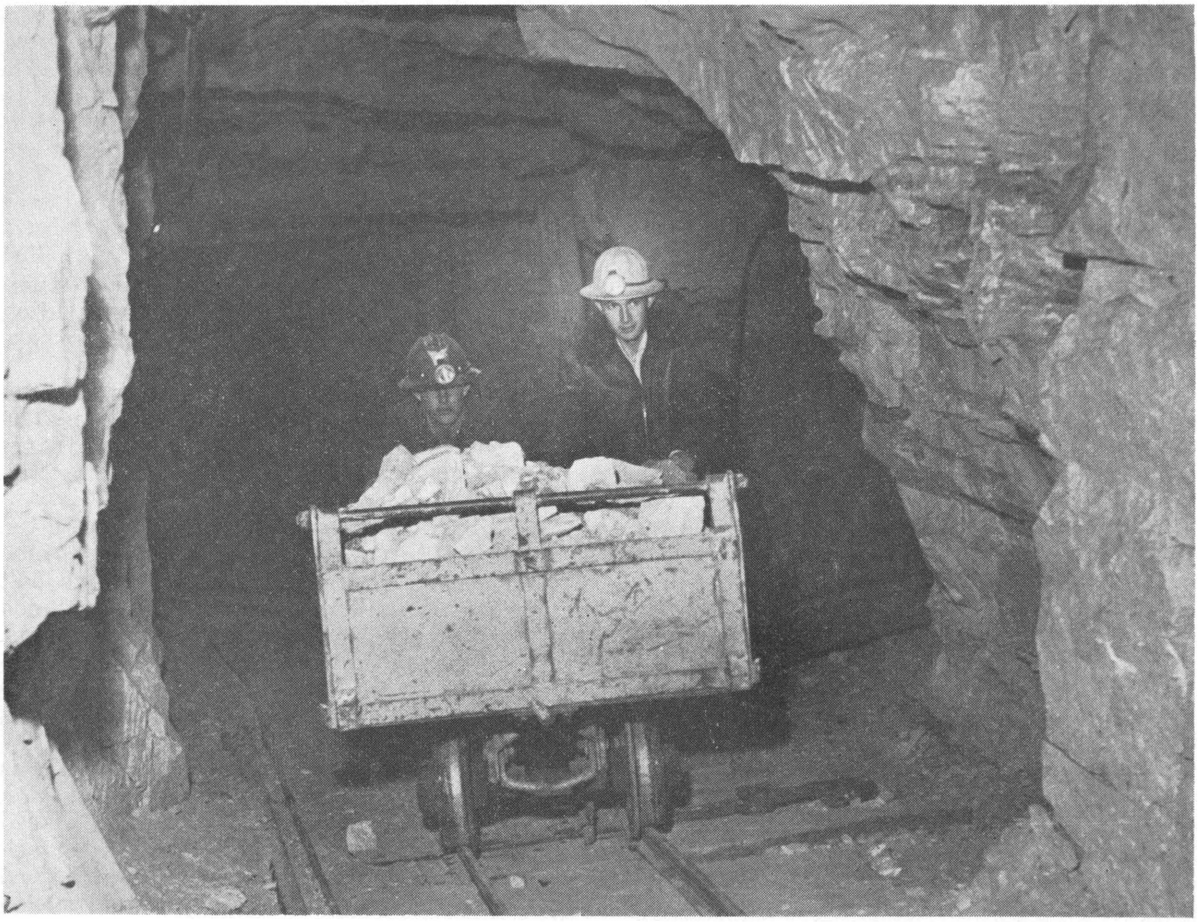

FIGURE 5.—Typical Interior View of Uranium-Vanadium Mine, Showing Rock Wall and Hand-Operated Ore Car.

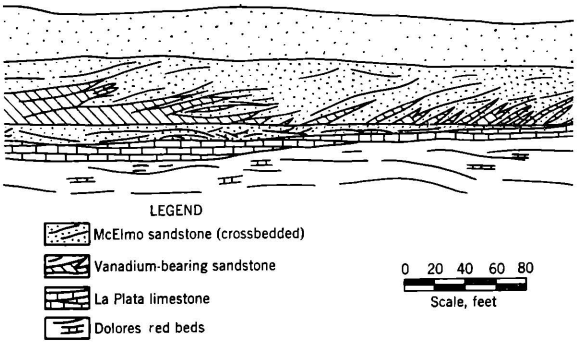

FIGURE 6.—East-West Cross Section, Showing Ore Body.

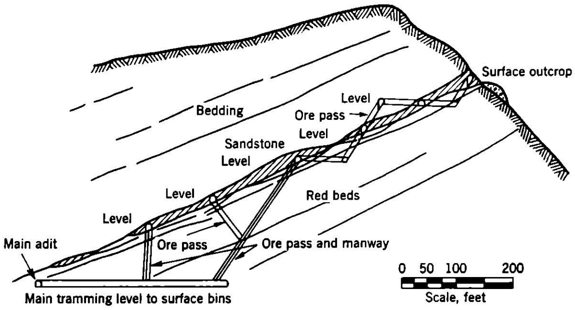

FIGURE 7.—Section of Mine Workings, Showing Method of Development.

uranium mine, vanadium of uncommercial grade is found in the ore. It is interesting because this mine is an open-pit operation.

Intensive exploration by The Anaconda Co. in the Grants area of New Mexico in 1950 led to the discovery of the Jackpile deposit. This deposit was found by a systematic program of aerial prospecting in which radiometric anomalies were carefully plotted on geologic maps.

The Jackpile ore occurs in irregular, tabular-shaped carbonaceous sandstone bodies. The two ore-bearing horizons range in thickness from a few inches to 20 feet or more and sometimes are separated by low-grade or barren sandstone as much as 30 feet thick. When this barren bed is absent, the mineralized sandstone may reach a thickness of 50 feet or more.

Lateral dimensions of mineralized members are roughly 1,000 by 6,000 feet with an overburden of 100 to 300 feet.

Early exploratory drilling revealed an ore body about 250 feet wide, 800 feet long, and a few feet to as much as 50 feet thick. Overburden averaged about 110 feet. Dimensions of the ore body were determined by drilling on 50-foot centers. Rock samples were taken and radiometric analyses made. The radiometric results were augmented by chemical analyses of samples taken from mineralized horizons.

To substantiate the drilling results, three tunnels were driven. One was driven 30 feet below the ore with certain drill holes as targets. These headings were large enough to use a diesel tractor-loader. Raises were driven through the ore when the drill-hole objectives were reached. Bulk samples were shipped to Anaconda's Bluewater plant for analysis and metallurgical testing.

Underground exploration gave information on the type of ground, supports needed, water problems, and working conditions, which was necessary to evaluate and plan a mining operation.

In spite of a ratio of waste to ore of about 8 to 1, it was decided to mine the deposit as an open pit, since only 60-percent ore recovery seemed practical by underground methods.

The overburden was removed within 20 to 25 feet of the mineralized horizon with 2½-yard diesel shovels and benches cut at 40-foot intervals. After the remaining overburden was removed, limited ore production was started. It was difficult to control grade owing to the spotty nature and abrupt changes in the ore body.

Mining faces ranged from 5 to 20 feet high. Blasting was done with 40-percent free-running bag powder in rotary holes and 1⅛-inch 40-percent dynamite in jackhammer holes. Waste material was removed by a 2-yard diesel tractor loader into 6-ton gravity dump trucks. A front loader was used to load ore-bearing material directly into high-way type trucks of 15-ton capacity for transport to the mill. As operations increased, added equipment included larger 22-ton end-dump trucks for waste disposal.

Exploratory drilling on an extended grid pattern north of the known deposit revealed a larger ore body. Procedures used in developing the first mine were utilized to start a second open-pit mining operation.

Early in 1955, two 5-yard electric shovels and associated equipment, capable of moving 700,000 cubic yards of material a month, were obtained. It was estimated that 15 million cubic yards of waste stripping was needed to prepare for additional mining operations.

It became evident that enough ore was present to warrant construction of a railroad spur line from the Sante Fe main line to the mine—a distance of about 4½ miles. Double track was installed at the loading sight, with switches and crossovers to handle the cars.

Enough ore was found in the area between the two pits to justify connecting them. The pits were also connected to aid in transporting the ore directly to the crushing and loading plant.

Loading equipment comprised an 80-ton hopper, a 48-inch pan feeder, a 42- by 48-inch jaw crusher, and a 425-foot by 48-inch belt conveyor. Supplemental equipment included a weightometer with remote-control stations, and a system of lights, signal horns, and electrical control switches which enabled three men to crush and load about 5 cars an hour.

When Anaconda's mill at Bluewater was completed early in 1956, mine production was increased. Additional equipment placed in service included a 5-yard electric shovel, a 500-kilowatt mobile powerplant, a 3-yard diesel shovel, several 22-ton dump trucks, three rotary air blast drills, a rubber-tired bulldozer, fuel trucks, and other equipment. Ore was produced (1956) with two 1½-yard shovels and four 22-ton trucks. The remainder of the equipment was used in stripping.

Initially, mining operations were controlled by exploratory-drilling results. On waste benches above the mineralized zone, supplementary samples were drilled by truck-mounted rotary air-blast drills on narrow sections which had been established throughout the area. Spacing of holes ranged from 25 to 50 feet, depending on the data obtained from the original drilling. Rock samples from these holes were taken every 5 feet throughout the ore body. Results from radiometric tests were plotted and correlated with all other information. Where radiometric results were doubtful, chemical analyses were made.

The next part of Anaconda's development program was the disposal of the material that rested on top of the low-grade horizon above the ore. To determine the depth of overburden, 4¼-inch-diameter blast holes were drilled on 8- to 12-foot centers. Holes were probed by counters to determine the limits of the ore, and waste was stripped.

When stripping operations were completed, the ore was sampled, shipped, and stockpiled.

Climax Uranium Co.—One of the larger uranium-vanadium ore producers of the Climax Uranium Co. has been the G–1 mine.

Ore in the G–1 mine is in sandstone lenses, which are generally cross-bedded and massive and vary in thickness. Carnotite, the main type of ore, is often associated with carbonaceous material.

The main entry, through which the entire output was hoisted before 1958, was 286 feet long and 8 by 8 feet in cross section. This entry was driven on a minus 15° grade to bottom at the main ore body. The first 90 feet of the incline was broken by drilling and blasting one long V-cut round from the surface. Holes in the round were wagon drilled progressively deeper along the incline to establish grade.

The first 100 feet of the incline was timbered with 8- by 8-inch timbers lagged at the back. The remainder of the incline was driven through sandstone which stood well without support. Approximately 110 feet below the surface and after the incline had intersected the ore horizon, an 8- by 8-foot tracked haulageway was continued on a minus-3-percent grade for 160 feet. Haulageways were cut beneath the southwesterly dipping ore, and at its end the track was 4 feet lower than the bottom of the ore. Ore was loaded into a Granby-type mine car and hoisted to the surface.

To follow the better ore exposures, headings about 8 feet wide and 8 feet high were driven out from the tracked haulageway. Headings were widened into rooms where the ore widened. Some spans of 60 feet or more stood several years without sloughing. Mine workings assumed a pattern of open stopes with pillars in random arrangement after headings and rooms became interconnected.

In the first advance, no roof support was used, but timber support was used later when some of the ore pillars were removed.

Other small ore bodies on the down-dip fringe of older stopes have been developed through 5- by 7-foot headings from a second entry. When drifting linked the two inclines, the natural ventilation in the mine was improved.

As is common practice in other uranium-vanadium mines, drilling was done with air-leg-mounted drills using 5- and 6-foot lengths of 7/8-inch hexagonal steel. Hard-surfaced or tungsten carbide bits were used to drill the rock. Heading rounds in sandstone were broken with a 26-hole pattern about a 3-hole triangular burn cut and charged with 1 1/8- by 8-inch cartridges of 45-percent semigelatin dynamite. In mudstone, 35-percent explosive was generally used. Stope rounds were drilled to break 50 to 60 tons of ore at a time.

Development headings in the G–1 mine were driven at least 7 to 8 feet high to accommodate trackless diesel-powered equipment underground. Front-end tractor loaders were used to load rubber-tired haulers. From the haulers, ore was dumped directly into a 4-ton Granby mine car for hoisting to the surface.

On the surface, the mine car was tipped to empty on the ground. A crawler-mounted loader was used to move waste to a dump area and to load ore trucks for the 50-mile haul to the Climax mill at Grand Junction, Colo.

Low-pressure ventilation was provided in the mine by a 4-foot-diameter, 20,000-cubic-foot-per-minute disk fan exhausting through a 110-foot, 5- by-6-foot timbered raise. Electric power was provided by a continuous-output diesel-electric unit.

METALLURGY

Preparation of crude vanadium-bearing ore for recovery of the metal oxide is a prerequisite to any extractive method. The preparation of ore varies somewhat from mill to mill.

Processing of mine-run ore starts when it is unloaded from trucks into coarse-ore bins at the mill. From the coarse-ore bin, usually an apron ore-feeder belt transports the ore to a grizzly. Oversize pieces of ore are fed to a crusher, and the crushed ore is conveyed with the undersize to a vibrating screen. The material passing through the screen is transported by belt to a fine-ore bin, and the oversize is crushed to less than a 2-inch size and also transported to the fine-ore bin. Just before the ore enters the fine-ore bin, samples are taken to determine its quality. From the fine-ore bin, the ore is weighed on a continuous weighing device and fed at a controlled rate to a ball or rod mill, where it is ground to the proper size and sent to the extractive circuits of the mill.

EXTRACTIVE METALLURGY

Commercial treatment of vanadium-bearing ores to retrieve the metal oxide content is not identical in all plants. Several extractive methods, including ion exchange and solvent extraction, which separate both uranium and vanadium from combined circuits, are used at domestic mills. In addition to the commercial extractive methods for recovering vanadium oxide, several experimental processes have been developed.

Recovery of Vanadium from Carnotite and Roscoelite.—Methods used to recover vanadium from carnotite and roscoelite ores in the quarter century before 1948 were based on a salt roast in which the ores were ground to about minus 14-mesh, mixed with 6 to 7 percent by weight of salt, and roasted at a temperature ranging from 825° to 850° C. in multiple-hearth roasters (*126*). The resultant calcine was quenched in water or a sodium carbonate solution to extract the vanadium, which had been converted to a soluble sodium vanadate by the salt roast.

Vanadium was recovered from the leach solution by adjusting the pH to 2.5 to 3 with acid, then heating and stirring the solution which precipitated a product known as "red cake" or sodium polyvanadate. Filtration, washing, and fusing with a direct flame yielded fused vanadium pentoxide containing over 86 percent V_2O_5.

In the 1940's, when uranium supplies became important to National Defense, vanadium mills were expanded and flowsheets changed so that recovery included uranium. Methods for recovering uranium in conjunction with vanadium had been known for some time but had never been applied on a large milling scale. One company, United States Vanadium Co. (now Union Carbide Nuclear Co.), which pioneered the recovery of both uranium and vanadium, utilized a water and acid leach process (fig. 8), followed by an acid leach and liquor purification to recover uranium. This process was used at its old Rifle (new mill constructed in 1958) and Uravan, Colo., plants. The Vanadium Corp. of America installed a carbonate leach-fusion method (fig. 9) at its Naturita (closed in January 1958) and Durango, Colo., mills.

In circuits utilizing a water leach for vanadium dissolution, water leach tailings were dewatered and given an acid leach, which dissolved 90 to 95 percent of the uranium with 50 or more percent of the remaining vanadium and some alumina, silica, iron and other acid-soluble components of the calcine. This solution was then neutralized with caustic or ammonia to a pH of approximately 6.0, which precipitated a green sludge. The sludge consisted of iron, alumina, silica, and other acid-soluble hydrates and contained all of the uranium and vanadium. Each ton of ore treated yielded approximately 50 to 100 pounds of green sludge. The sludge was then filtered from the solution and redissolved by heating it with sulfuric acid and an oxidizer such as sodium chlorate.

This step of sludge formation and redissolving was primarily a dewatering and concentrating operation, which decreased the amount of solution necessary to be handled. After the green sludge had been redissolved, the acid liquor was again neutralized with a base (using pH control under proper conditions), and the vanadium was precipitated and removed as iron vanadate at a pH range of 2.5 to 3. Iron vanadate was returned to the salt roasting operation.

After the vanadium was removed, the pH of the liquor was increased to about 9 by neutralizing the solution with sodium carbonate. The alumina, silica, iron, and other miscellaneous hydrates were again precipitated as an alumina sludge, and the uranium remained in solution as the uranyl tricarbonate complex. This alumina sludge was filtered from the solution and washed to remove as much of the uranium-containing liquor as possible.

The filtrate, containing little more than the uranyl tricarbonate complex, was acidified and boiled, which drove off the CO_2 and broke up the complex. With the addition of a base, the uranium precipitated as a relatively pure salt.

In circuits in which a sodium carbonate leach was used to dissolve the vanadium, quenching the calcine in a sodium carbonate solution dissolved about 75 to 80 percent of the vanadium. A longer contact time in hot solution dissolved approximately 75 to 85 percent of the uranium. The sodium carbonate solvent was selective for both uranium and vanadium and dissolved a minimum of other materials in the calcine. The uranium was recovered as a synthetic carnotite precipitate (sodium uranyl vanadate) by adjusting the pH of the carbonate liquor to about 6.0 with H_2SO_4 and boiling the solution to remove the CO_2. Synthetic carnotite was precipitated and removed by filtration. Vanadium in excess of the quantity needed to precipitate the uranium remained in the filtrate and was recovered by "red cake" precipitation. The synthetic carnotite cake was given a reducing fusion with a flux containing salt, soda ash, and sawdust or fuel oil. This fusion formed the water-insoluble black uranium oxide and water-soluble sodium salts of vanadium and other amphoteric impurities. The melt was allowed to cool; then it was leached with water, leaving the concentrate, black uranium oxide, which was filtered from the leach liquors. In carbonate leaching, an impure uranium concentrate was precipitated and purified by fusion.

One mill, at Monticello, Utah, leached the calcine in sodium carbonate solution at 90° C.

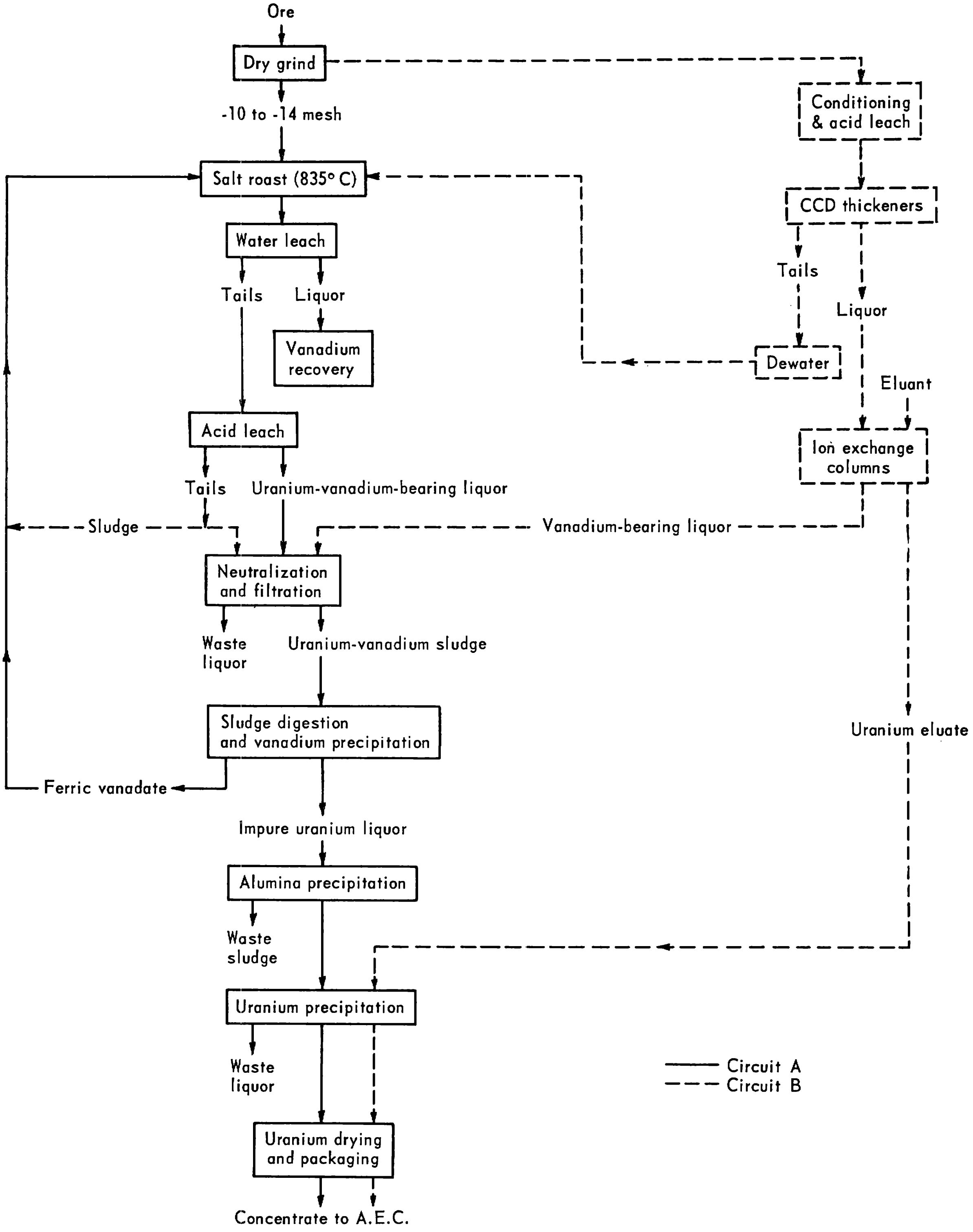

FIGURE 8.—Flowsheet of Water-Acid Leaching and Ion Exchange Process Used at Union Carbide Nuclear Corp. Mill, Uravan, Colo.

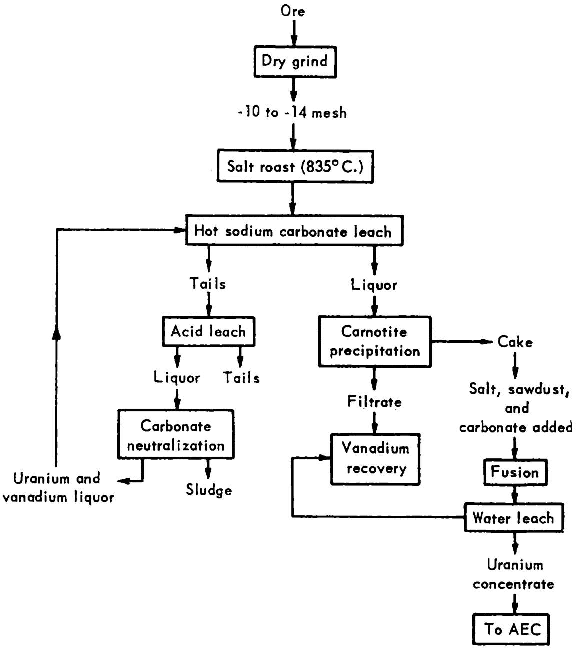

FIGURE 9.—Flowsheet of Sodium Carbonate and Acid Leach Method of Vanadium-Uranium Recovery.

for enough time to solubilize about 90 percent of the uranium and discard the resulting tailings. Mills at Durango and Naturita did not do this; to make a throwaway tailing, calcine from the carbonate leaching was dewatered and given a leach with a dilute sulfuric acid solution, which resulted in recoveries of an additional 15 to 20 percent of the uranium and vanadium mill-feed values lost in the carbonate leach tailings. The acid liquor was then neutralized with an excess of sodium carbonate, and the resulting alumina sludge was filtered from the sodium carbonate liquor and washed. The liquor contained the uranium and vanadium values which were used for the carbonate mill solution.

No circuits, except those utilizing a water leach or a sodium carbonate leach, have proved as suitable for recovering uranium and vanadium.

However, several other methods have been developed for recovering uranium in the last 6 or 7 years, which also include vanadium recovery. One method was the phosphate precipitation process, used and later abandoned by Climax Uranium Co. and Vitro Chemical Co. The process was based upon the fact that uranous phosphate will selectively precipitate from acid liquors giving a much higher grade uranium cake than can be obtained by neutralizing the acid liquor. The uranous phosphate was precipitated by reducing solutes in acid liquors with a reducing agent, such as iron or aluminum, and having enough phosphate in the liquor to combine with uranous ions as they were formed.

Climax Uranium Co. formerly used a salt roast and water leach to recover vanadium, as the mill feed was typical Colorado Plateau carnotite ores. This process included a sand-slime separation step, which concentrated approximately 70 percent of the values into the 150-mesh slime fraction that comprised 30 to 40 percent of the weight of the ground ore. This process decreased by approximately two-thirds the tonnage of ore it was economic and necessary to salt roast for vanadium solubilization. The method also included an ore-conditioning step, in which the residual acid in the uranium-barren liquor was used for neutralizing the lime in the raw millfeed pulp from the wet-grinding circuit. This step neutralized the barren liquor and precipitated all the contained uranium and vanadium values into the pulp, also other soluble materials such as aluminum, silica, and iron. These precipitated values followed the slime part of the ore and the salt-roast dehydrates and made the alumina and silica insoluble, preventing a build-up of these impurities in the mill circuit.

The calcines were water leached for vanadium recovery, then acid leached to recover uranium and scavenge for the acid-soluble vanadium. Sands, which were initially separated from the slimes, were acid leached for the same purpose. These acid liquors were sent to the phosphate precipitation step for uranium removal.

Vanadium recovery by solvent extraction was started in 1956 by Climax Uranium Co., Grand Junction, Colo., to replace the phosphate precipitation method. At the Climax mill, the flowsheet provides for extraction of vanadium, followed by acid leaching and solvent extraction of uranium. At the Kerr-McGee mill, Shiprock, N. Mex., the ore is acid leached; this process recovers practically all of the uranium but only 30 percent of the vanadium. Both metals are recovered in two steps by solvent extraction, the uranium first and the vanadium next, as shown in figure 10.

Recovery of Vanadium From Wulfenite.—At Tiger, Pinal County, Ariz., Mammoth-St. Anthony, Ltd., from 1935 to 1944, carried on a unique operation involving the commercial production of vanadium from a complex ore which also contained molybdenum, gold, silver, and lead (*43*, *52*).

In this process the complex ore was first smelted with soda ash and coke, yielding a molybdenum-vanadium rich slag which was

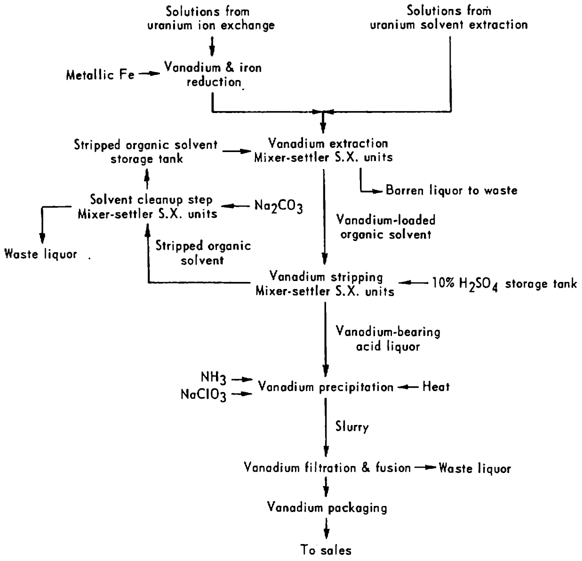

FIGURE 10.—Flowsheet of Vanadium-Uranium Recovery by Solvent Extraction.

treated at the plant. The slag was handsledged, crushed, and ground with water in a rodmill to dissolve the sodium vanadate and molybdate. After the solution was filtered, part of it was evaporated by smelter waste heat to dry sodium molybdate-sodium vanadate salt; the remainder of the solution was used in the separation of molybdenum from vanadium.

The unused solution was mixed with the combined salt and agitated 8 hours. In this treatment, molybdenum was dissolved and vanadium precipitated. Filtering removed the residue which contained 20 to 25 percent V_2O_5.

The solution containing molybdenum was treated with enough lime and calcium chloride to precipitate a low-grade calcium-molybdate-silicate product, which was stored for re-treatment. The filtered solution was then treated with calcium chloride which precipitated molybdenum as a high-grade calcium molybdate.

Recovery of Vanadium From Chromite.—Vanadium occurs to a limited extent in chromite ore, and at some plants making chromium compounds it is recovered by acid precipitation. The method was described in a trade magazine (*84*) and was the subject of a patent (*90*). According to Chemical Abstracts (*91*): [7]

> Partially neutralized leach liquors (pH about 8.5) from soda-ash roasting of chrome ores contain about 1 part V to 1,000 parts Cr: $PbSO_4$ is added to precipitate the V and a small part of the Cr as Pb vanadate and chromate. The purified liquor is processed for chromate production, and the V and Cr in the cake are extracted with cold dilute H_2SO_4 (about 1:3), $PbSO_4$ being recycled. V in the acid ext. is pptd. by adding alk. leach liquor to a pH of 2, heating to 90°, and agitating gently for 3 hours; the ppt. consists of colloidal $Na_2H_2V_6O_{17}$ and contains about 85 percent V_2O_5. The V-free acid liquor is used to neutralize alk. leach liquor from the soda-ash roast.

Recovery of Vanadium From Crude Petroleum.—Vanadium is present in small quantities in various crude petroleums. Some Venezuelan crude oils contain as much as 0.06 percent V_2O_5; Mexican crude contains 0.02 to 0.044 percent V_2O_5 and midcontinental crude, 0.01 to 0.02 percent. The flue dust that collects in the boilers of tankers which burn Venezuelan fuel oil was reported to contain 20 to 40 percent V_2O_5. Some of the flue dust has been salvaged and converted to vanadium pentoxide. An analysis made of a sample of flue dust from the boiler tubes of a ship burning Venezuelan fuel oils was as follows:

	Percent
V_2O_5	35.28
Al_2O_3	.50
SiO_2	2.50
Fe_2O_3	4.80
MoO_3	.08
NiO	6.01
CoO	.29
SnO	.37
ZnO	.14
CaO	1.05
MgO	1.90
K_2O	.49
Na_2O	13.61
SO_3	29.94
Cl_2	(1)
Ignition loss	2.84

[1] Trace.

A patent (*41*) has been issued for the recovery of vanadium from crude oils. According to Chemical Abstracts (*40*): [8]

> A method is employed which involves atomizing the oil and effecting its combustion in a furnace continuously producing flue-ash particles substantially all not larger than 200 microns in diameter, separating the flue-ash particles from the flue gases into a finer portion containing flue-ash particles less than approximately 40 microns in diameter and a coarser portion containing flue-ash particles greater than approximately 40 microns in diameter, continuously recycling the coarser portion to the combustion space and recovering the vanadium from the finer portion.

Recovery of Vanadium From Phosphate Rock.—From 1941 to 1954, The Anaconda Co. recovered vanadium (fig. 11) at its reduction

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[7] Reprinted with permission from the American Chemical Society.

[8] See footnote 7.

plant at Anaconda, Mont., in connection with the treatment of phosphates under a patented process (*36*), which is described briefly as follows (*46*):

> The phosphate rock going to the plant contains approximately 0.3 percent V_2O_5, corresponding to 0.16 percent vanadium. The rock is treated with sulfuric acid, primarily for the purpose of leaching out the phosphoric acid. At the same time, approximately 65 percent of the vanadium contained in the rock goes into solution together with the phosphoric acid. This is precipitated as phosphovanadic acid by treating the solution with sodium chlorate. The yellow crystalline precipitate is separated by settlement. It contains phosphorus, iron, alumina, lime, and other impurities. By treatment with milk of lime and soda ash under carefully controlled conditions, the vanadium is obtained in a substantially pure sodium vanadate solution, from which vanadium pentoxide, V_2O_5, is precipitated by the addition of sulfuric acid. This is the "red cake" precipitate which upon drying is ready for the market.

A method for recovering vanadium from impure phosphorus-vanadium material, which comprises treating the material in an aqueous medium with ammonia and an alkali metal hydroxide, is the subject of a patent (*49*).

Recovery of Vanadium From Western Phosphate Rock.—The Bureau of Mines conducted small-scale laboratory tests on samples of western phosphate to determine the amount of vanadium that could be recovered from ferrophosphorus as a byproduct of smelting operations. Results of these tests were given in Report of Investigations 4822 (*80*) and U. S. Patent 2,654,655 (*93*).

Crucible smelting tests at the Northwest Electro-development Laboratory of the Bureau and a pilot-plant test in electric smelting of western phosphate rock for the Westvaco Chlorine Products Co. by the Tennessee Valley Authority demonstrated that the small vanadium content of the rock concentrates in the ferrophosphorus byproduct of phosphorus smelting.

Several methods of treating vanadiferous ferrophosphorus were tested. Attempts to separate vanadium as a carbide dross by saturating molten ferrophosphorus with carbon were unsuccessful. Attempts to volatilize phosphorus from ferrophosphorus, with and without additions of sulfur in different form, had limited success, but elimination of phosphorus was not thorough. Another method that gave encouraging results was the fusing of vanadiferous ferrophosphorus mixed with soda ash under oxidizing conditions. A slag product of the fusion reportedly contained most of the phosphorus and vanadium as water-soluble sodium phosphate and virtually water-soluble sodium vanadate. The leach residue was reroasted with soda ash and salt after leaching the sodium phosphate from the slag. To extract the vanadium, the roasted product was leached again with water. Still another method which showed promise was a brief testing in a small experimental converter of the oxidization of vanadium and phosphorus into a slag by blowing the mixture with air.

Of the various methods for treating vanadiferous ferrophosphorus, the leach roasting process (fig. 12) was the most promising. In this experimental test, the vanadiferous ferrophosphorus was roasted with soda ash and salt, then water leached to extract vanadium and phosphorus. Phosphorus crystallized from the clarified leach solution as trisodium phosphate. The primary crystals in this process were freed of vanadium by dissolving them in water and then recrystallizing them. Vanadium in the phosphorus-free solution was recovered by hydrolysis as vanadium pentox-

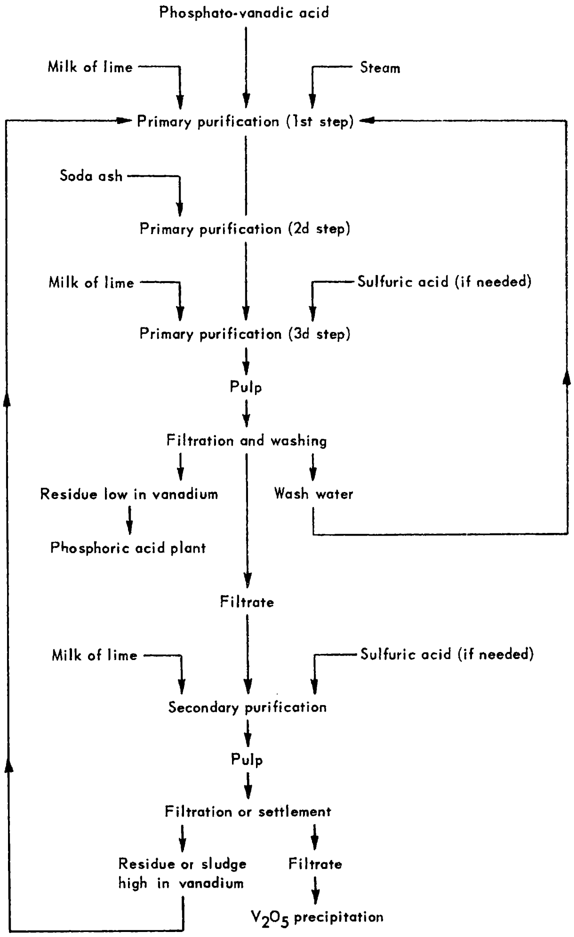

FIGURE 11.—Flowsheet Showing Recovery of Vanadium From Phosphate Rock as Once Used by The Anaconda Co., Anaconda, Mont.

ide or "red cake." Recovery was as high as 95 percent vanadium and 96 percent phosphorus from the ferrophosphorus. In other tests only 85 percent of the vanadium was recovered in the final "red cake" and 87.4 percent of the phosphorus as trisodium phosphate.

As only one company, The Anaconda Co., has recovered vanadium from phosphate rock and as vast reserves of phosphate rock and shales remain undeveloped in Montana, Idaho, Wyoming, and Utah, the experimental procedures developed by the Bureau of Mines were significant as possible extractive methods to obtain future supplies of vanadium.

Recovery of Vanadium From Bauxites.—The extraction of vanadium from bauxites in the Bayer process has been described in abstract form (*68*) as follows:

> Salts containing V_2O_5, P_2O_5, As_2O_5, and Na_2O are recovered from decomposed aluminate liquors from the Bayer process by crystallization at 20°–25°, and washed to eliminate Na aluminate. The salts are then suspended in an amount of water equal to their weight. After heating to 70°–80°, the alky. is at least partially neutralized with H_2SO_4 or H_3PO_4. The solution is allowed to cool and the crystallized salts containing the P and As are filtered off. From the filtrate the V is precipitated as ammonium metavanadate or as Na hexametavanadate. By calcination of these V salts in a closed vessel, the lower oxides of V, such as V_2O_4 and V_2O_3, are obtained. These oxides are reduced in the presence of Fe with Al at a high temperature to produce ferro-V, containing 50–60 percent V and less than 1 percent Al. This alloy melts at 1,480°–1,500°.

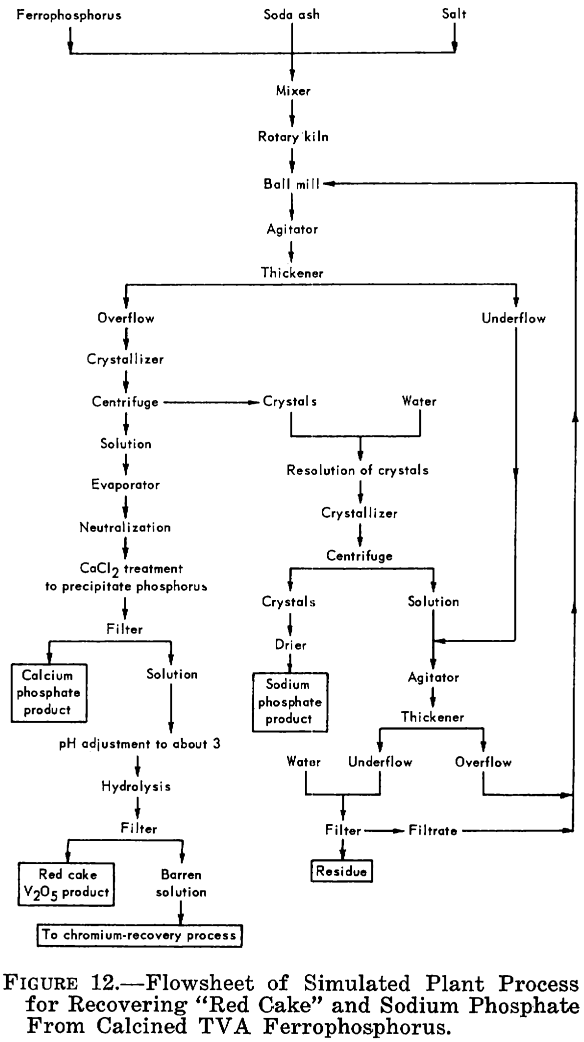

FIGURE 12.—Flowsheet of Simulated Plant Process for Recovering "Red Cake" and Sodium Phosphate From Calcined TVA Ferrophosphorus.

Recovery of Vanadium From Titaniferous Magnetites.—Research has been done in various countries on the recovery of vanadium from iron ore, and the literature contains references to many articles on the results of such work. In general, the methods of recovering vanadium from titaniferous magnetites fall into two categories—metallurgical and chemical.

The recovery of vanadium from titaniferous magnetites has been investigated by the Bureau of Mines (*51, 83, 86*).

Investigations revealed that most of the vanadium in the MacIntyre ore (Tahawus, N.Y.) could be recovered in pig iron that could be blown in a converter to produce a slag containing large enough percentages of vanadium for recovery.

In the process, the presence of metal shot made it difficult to determine the quantity of vanadium in the slag. Thirteen slags were ground to pass a 200-mesh screen. This powdered slag was then passed through a magnetic tube concentrator to separate magnetic and nonmagnetic fractions. The vanadium content of the metal-free slag or nonmagnetic meterial averaged 0.02 percent but ranged from 0.01 to 0.04 percent. Many of the apparently metal-free slags assayed 0.02 percent vanadium.

During specific periods of blast-furnace operation on the all-sinter burdens the hearth built up. Additional material may have accumulated on the bosh walls in the fusion zone. Part of this material was fluxed and carried away by more fluid slags during certain periods of furnace operation. An indicated recovery of 127.4 percent of the vanadium in the metal for one period was accounted for by this slagging action. Likewise, more vanadium was recovered in the metal than was charged to the furnace in another period of operation. For the entire test, 87.3 percent of the vanadium was recovered in the metal and 3.8 percent remained in the slag. These two figures accounted for 91.1 percent of the vanadium charged and indicated a loss of 8.9 percent.

Data were not obtained on the amount of stock blown out as dust, but little material accumulated in the single-cone dry-dust catcher during the test.

Although making an accurate balance is difficult when dealing with small concentrations of vanadium, the results of the experimental tests indicate that most of this element will enter the metal. Therefore, one of the main problems in using vanadium-bearing titaniferous sinter involves the limits that TiO_2 in the slag may impose on the proportions of sinter in blast-furnace burdens. It was reported that an all-sinter burden could be smelted by adding silica as a flux to increase the slag volume and dilute the TiO_2 without greatly lowering the vanadium content of the metal. Such a practice would reduce pig-iron output.

Other Bureau of Mines researchers developed a process for recovering titania, iron, and byproducts from two types of titaniferous iron ores. According to the published report (*86*):

> Tahawus magnetite from the MacIntyre mine at Tahawus, N.Y., was successfully treated as follows: (1) the ore was roasted at 1,050° to 1,080° C. with carbon and soda ash, thereby reducing the iron to metal sponge and retaining the titania in the slag. (2) The metallic iron was separated, after wet grinding, by magnetic or gravity means. (3) The slag fraction was air roasted at 850° C. and leached with NaOH to recover Na_3VO_4. (4) The leached solids received a dilute H_2SO_4 leach to remove interfering impurities, chiefly Na_2O and SiO_2. (5) Titanium was dissolved from the leached solids of step 4 by a H_2SO_4 bake, followed by a water leach. (6) Titanium was precipitated by seeding and boiling the resulting solution. The spent liquor was used for the dilute H_2SO_4 leach in step 4.

Earlier experiments demonstrated that about 90 percent of the vanadium appeared in the slag after the reducing roast of the ore with carbon and Na_2CO_3. On subsequent water and alkaline leaches of the slag, little of the vanadium was dissolved.

Dilute H_2SO_4 leach of the slag readily extracted the vanadium, but recovery from this solution was hampered by the difficulty of separating the vanadium from large amounts of silicic acid and iron hydroxides.

It was concluded that to simplify recovery the vanadium should be obtained in a form soluble in an alkaline medium. According to the techniques used, a preliminary air roast of the ore with 15 percent of its weight of Na_2CO_3 at temperatures of 925° and 1,025° C. produced a clinker from which approximately 30 percent of the vanadium was extracted in an alkaline solution. By doubling the amount of Na_2CO_3, extraction was increased 50 percent. Table 14 gives results of the several tests.

TABLE 14.—*Extraction of V_2O_5 from Tahawus magnetite roasted*[1] *with $NaCO_3$ before reduction with carbon*

Run No.	Ore size, mesh	Na_2CO_3, grams per 100 grams of ore	Water-leach[2] time, hours	Extraction of V_2O_5, percent
1	−65	15	8	31.3
2	−65	30	8	56.7
3	−150	15	8	6.9
4	−150	30	2	17.5
5	−65	45	2	51.8
6	−65	[3] 30	2	41.0

[1] Temperature 925° C.; time, 2 hours.

[2] Temperature of leach, 60° C.

[3] This test also contained $NaNO_3$ equivalent to 5 percent of the weight of the ore.

During a study of the effects of refurnacing the nonmagnetic fraction of the sintered ore to improve the results of the dilute H_2SO_4 leach, it was found that a water leach of the refurnaced material extracted a greater percentage of the vanadium than was extracted before refurnacing. Additional work demonstrated that approximately 80 percent of the vanadium contained in the nonmagnetic fraction of the sintered ore was made soluble in hot 20-percent NaOH solution by an oxidizing roast at 850° C. Although studies did not include the investigation of the mechanism by which vanadium was solubilized by a reducing roast followed by an oxidizing roast, the combined treatment proved more effective than either an oxidizing or reducing roast of the ore alone. A similar process for treating certain types of vanadium-bearing ores has been patented in the United States (*73*).

A method for precipitating hydrous vanadium oxide (*58*) from an alkali vanadate solution consists of acidifying the solution to a pH value between 2.0 and 3.0 and boiling. The resulting precipitated hydrous oxide of vanadium, known as "red cake," is separated by filteration.

The procedure was not well adapted to other steps involved in the ore-treatment process because of the large quantity of NaOH and other compounds in the vanadate solution. Therefore, a recovery procedure was tried in which the concentration of sodium vanadate and other salts was built up in successive leaching cycles until it was possible to crystallize hydrated sodium vanadate salts from solution by controlling the temperature and causticity.

The following experimental procedure was used:

> Ten kilos of the nonmagnetic fraction of the sintered ore was thoroughly oxidized by roasting and rabbling at 850°. Twenty 500-gram batches were leached with 3,200 ml. of a recirculating solution, which was originally a 30-percent NaOH solution. Two hours stirring at the boiling temperature of the solution extracted the soluble vanadate, and the slurries were filtered while hot on 10-cm. sintered glass filters. The filter cakes were washed with enough water to replace losses, so that the volume of liquor for the succeeding cycle was 3,200 ml. Analytical samples were taken of the solution from each cycle, after making up the volume, and residues were analyzed once every four cycles.

From cycles 1 to 18, the concentration of V_2O_5 increased rather uniformly reaching a maximum of 6.6 grams per liter at the end of cycle 18. The concentration dropped 6.1 grams per liter at the end of cycle 20, owing to crystallization of a Na_3VO_4 hydrate on cooling.

With each cycle, the concentration of SiO_2 also increased but not as uniformly as that of V_2O_5. After cycle 6, crystals of a sodium silicate hydrate, tentatively identified as $Na_2SiO_3 \cdot 6H_2O$, were deposited. Solubility of this compound increased with temperature, like that of the sodium vanadates. This increased solubility did not interfere with crystallization of the sodium vanadates, as the concentration of SiO_2 was controlled by boiling the solution with the proper amounts of $Ca(OH)_2$ to form dicalcium silicate, which was removed later by filtration.

After reducing the silica concentration in a sample of the liquor from cycle 20 from 74.7 to 27.2 grams per liter by boiling it 1 hour with $Ca(OH)_2$, the solution was filtered and cooled to 25° C. Crystals tentatively identified as $Na_3VO_4 \cdot 12H_2O$ and $Na_3VO_4 \cdot 7H_2O$ were deposited. After separating the mother liquor, the crystals were washed with alcohol and analyzed.

The V_2O_5 solution was approximately 67 percent of that in all sinter processed at the end of cycle 18. Recovery was smaller than that obtained in single, small-scale extraction tests. It was thought that a more efficient washing technique would yield an extraction of 80 percent or more. Less than 1 percent of the Al_2O_3 and 10 to 12 percent of the silica were extracted by the recirculating leach. Total causticity in the final liquor had increased from 30 to 42 percent.

With certain modifications, the process described for Tahawus magnetite was successfully applied to a titaniferous iron ore from Iron Mine Hill near Woonsocket, R.I.

A method was developed in the laboratory by Back and others for successfully treating titaniferous magnetite ore from the deposit at Iron Mountain, Wyo. (*83*). The ore was roasted with 15 percent sodium carbonate to convert the vanadium to a water-soluble form and fix the soda for the subsequent electric-smelting step. Approximately 90 percent of the vanadium was recoverable in a product assaying 80 percent V_2O_5.

Recovery of Vanadium From Titaniferous Magnetites in Finland.—A new production process for recovering vanadium was developed by Finnish scientists and placed in operation at the government-owned mine and mill at Otanmäki, Finland (*107*).

> Magnetite concentrate, dried and cleaned by a permanent magnetic process, is mixed with sodium salt and reground in a ball mill. This concentrate is suitable for pelletization, which takes place in a pelletizing drum. With the aid of a proper amount of water, about 1-inch balls are rolled and fed into a pelletizing furnace. This is a round shaft furnace designed especially for the reaction between vanadium and sodium. For this reason the construction of the furnace differs noticeably from that of normal pelletizing furnaces. The burnt pellets are removed into a countercurrent leaching system. Hot water is used as leaching solution. The pregnant solution obtained contains 16–10 grams per liter of vanadium in the form of sodium vanadate. The leach pellets are sold as high-grade iron concentrate. In wooden tanks the vanadium is precipitated from the solution with sulfuric acid, resulting in a precipitate of vanadic acid. This is separated from the solution in pressure filters. By special methods the precipitate is cleaned of impurities before being smelted and cast into cakes. In this form the product is delivered to the market as smelted vanadium pentoxide, analyzing as follows:

V_2O_5	percent	90–92
SiO_2	"	1.0
P	"	.01
X	"	.01
As	"	.01
Na_2O	"	4.0

> The production during the first stage is calculated at about 600 tons of smelted vanadium pentoxide per year, a figure that will be doubled in 1957.

Recovery of Vanadium From Steel Plant Slags in Germany.—During World War II, Germany had no adequate supplies of vanadium. Their only sources of this metal were the iron ores of Salzgitter, Lorraine, and Luxembourg, which contained small quantities of vanadium. Methods for obtaining vanadium were worked out to recover the metal from the slags in steel plants using these ores. As Germany apparently was self-sufficient in respect to vanadium supplies, it must be concluded that their extractive processes were successful and economically feasible under wartime conditions. In fact, they not only obtained enough vanadium for wartime uses, but supplies were large enough to enable them to substitute vanadium for other nonferrous metals (*56*).

German iron ores contain about 0.1 percent or less vanadium; however, some of the Swedish iron ores available to the German iron industry contained slightly more than 0.1 percent vanadium. In practice, most of the vanadium in the ore went into pig iron, which was blown in the Thomas converter, producing a slag containing 1 percent or more vanadium. The slag was resmelted; the vanadium went with the iron, which was blown again, resulting in a slag containing about 10 percent vanadium; finally, this slag was treated at various chemical plants to recover the metal.

The Hermann Göring steel plant at Watenstedt used Salzgitter iron ores containing about 0.1 percent vanadium. Acid and basic iron produced in the blast furnaces of this steel plant contained about 0.3 percent vanadium. After experimental work on the large-scale production of vanadium-rich slag, operation of the Thomas converter plant was begun in mid-1942. With the Thomas converter, the slag resulting from blowing the pig iron averaged about 1.5 percent vanadium. Slag, along with dust or splittings from the converter and some Salzgitter ore, was charged into one blast furnace and resmelted, resulting in a pig iron rich in vanadium and phosphorous. Percentage analysis of the slag was approximately as follows: Vanadium 1.5; phosphorus, 9.0; manganese, 1.0; sulfur, 0.1; and carbon, 1.5. The slag was blown down in a converter with a fire-clay lining and a dolomite bottom, producing a dry slag. Average percentage analysis of this slag was reported as: Vanadium, 14.5; phosphorus, 9.5; calcium oxide, 2.0; silica, 0.01; manganese, 0.03; and sulfur, 0.1. This vanadium-rich slag was shipped to chemical plants to recover vanadium. The residual iron was sent to the blast-furnace works in Westphalia, where Thomas iron without vanadium was produced. Thomas slag, containing phosphorus but little or no vanadium, was sold as fertilizer slag. Production of vanadium-rich slag at the Hermann Göring works (Watenstedt) was reported as ranging from 50 to 100 tons of contained vanadium per month—a large part of the German production of vanadium-rich slags.

At the Röschling Steel Works, Volklinge, the iron ores used, which were thought to be Minette ores, contained 0.015 to 0.03 percent vanadium. Pig iron from smelting these ores reportedly contained percentages of the following: Vanadium, 0.10 to 0.15; phosphorus, 1.9 to 2.0; silica, 0.50; manganese, 0.50; carbon, 3.5; and sulfur, 0.05. At this plant, several methods of producing vanadium-rich slags were used.

The iron in the Röschling method was incompletely blown in an acid converter, producing a slag with the following percentage analysis: Vanadium, 1.4; iron, 39; silica oxide, 30; manganese, 8; and phosphorus, 1.4. This slag, together with raw ore, Thomas slags, and converter shot and splittings containing 0.5 percent vanadium, was resmelted in a separate blast furnace. Pig irons from this process contained the following percentages: Vanadium, 5.0; silica, 0.3; manganese, 1.3; phosphorus, 3.3 to 3.5; and carbon, 3.3. This iron was blown in an acid converter, producing a vanadium-rich slag with the following percentage analysis: Vanadium, 7 to 8; iron, 16.0; phosphorus, 1.25; manganese, 21.0; calcium oxide, 2.5; and silica oxide, 23. This slag was then sent to a vanadium plant for treatment.

Although the practices differed in detail in the several plants recovering vanadium, basic procedures were the same. Vanadium-rich slags were ground to 0.15 millimeters and roasted at about 800° C. with soda ash (Na_2CO_3) or sodium chloride ($NaCl$), producing a water-soluble vanadate which was leached with water, then the sodium vanadate (vanadium oxide) was precipitated with acid. Despite the range in composition of the various vanadium slags, favorable results were obtained during the war. A common difficulty was the use of too high roasting temperatures, which caused sintering or melting of the slags. Where recovery was not satisfactory, adding a little red iron oxide or silica compound or mixing the slags to obtain the desired composition gave better results.

Because there was insufficient time during the war to construct vanadium roasting plants, the existing sulfur roasting installations were utilized. Multiple-hearth and kiln roasters were used; however, basically these were not thought satisfactory, as the heating gases go counter to the ore (slag) through the roaster. Dust losses were negligible since the slag was heavy.

The vertical, multiple-hearth roasters used by the Germans were probably similar to the Skinner roaster used in treating the vanadiferous sandstone ores in the United States. Roasters in Germany were said to have a capacity of approximately 10 tons a day, a diameter of 7 meters, and 7 hearths. The feed was continuous. About 4 to 5 hours was required for a particle to pass through the furnace. Apparently it was desirable to keep the three middle hearths hottest, approximately 800° C.; however, occasionally the iron in the slag burned, raising the temperature enough to agglomerate the ground slag and prevent satisfactory reactions. When this occurred, the leach would yield only 30 percent of the vanadium in the slag and the roasted slag would be returned to the blast furnace to enrich new slags.

Roasting kilns reportedly had a capacity of 20 to 40 tons a day and operated continuously; a particle would pass through the kiln in approximately 3 hours.

When the roast was hottest, a quick-leaching quench was shown by experiments to yield the highest recovery, but this was not practicable on a commercial basis. The roasted material was allowed to cool and leached with water at about 100° C.

In Germany, the slag was reported to be leached only once. By German standards, the vanadium was "either soluble or insoluble," so that only one leach was effective. Leaching time ranged from 10 minutes to 1½ hours in different plants.

Because the leach dissolved the phosphorus in the roasted slag, calcium-bearing solutions were added to make a calcium-phosphate precipitate and the vanadium-bearing solution was filtered off.

Sodium vanadate was precipitated by adding either H_2SO_4 or HCl, bringing the pH to 2.8 to 3.2 The precipitate normally contained 48 to 53 percent vanadium (85 to 94 percent V_2O_5) and 4 to 10 percent Na_2O, including a trace of phosphorus.

The precipitated vanadium oxide was converted to ferrovanadium.

During the last part of the World War II, about 4,000 tons a month of vanadium-rich slags reportedly were treated in Germany.

Two other methods were used in Germany during the war to produce vanadium. One was the Burback method, in which about 5 percent of the liquid iron was blown for 3 or 4 minutes, producing a slag containing 0.5 to 0.8 percent vanadium. In this method, slag was mixed with cupola and open-hearth slags, but no ore, and charged into separate blast furnaces, resulting in iron containing 0.5 to 1.0 percent vanadium, 4 to 7 percent phosphorus, and 2 percent carbon. The iron was blown in basic converters, producing a slag containing 7 to 8 percent vanadium, which was then sent to a vanadium plant.

Another method of producing vanadium was the Völkligen process, which used a Frisch trommel instead of a double blow because of the plant layout. In this process, splittings (from basic converters) containing 0.3 to 0.5 percent vanadium and 70 to 80 percent iron were charged into a small blast furnace with a little ore and lime, together with residue from the vanadium extraction plants. After enough splittings were accumulated, the furnace was run intermittently. The smelted iron contained approximate percentages of constituents as follows: Vanadium, 0.65; phosphorus, 7.0; silica, 0.3 to 0.5; manganese, 1.5 to 4.0; and carbon, 2.0.

The iron was blasted with air in a runner that fed the trommel, resulting in slag containing 7 to 8 percent vandium which was sent to vanadium plants for further processing.

These slags were reportedly treated by two methods: (1) Silicious slags were treated with sodium carbonate to form sodium vanadate, which was leached with water and precipitated with hydrochloric or sulfuric acid as vanadium oxide; (2) basic slags were washed with sulfuric acid, roasted with sodium chloride before water extraction, and boiled with lime to precipitate calcium vanadate.

During World War II, eight steel plants in Germany produced vanadium-rich slags: Hermann Göring, Watenstedt; Vereinigte Stahlwerke-August Thyssen, Hütte; Mannesmann, Röhrenwerke; Röesch, Dortmund; Klöchner-werke, Hagen-Haspe; Gutehoffnungs Hütte; Röschling Steel Works, Völklinger; and Rheinhausen-Krupp.

Plants treating slags from these steel plants were: Gessellschaft für Electrometallurgie, Nurnberg; I. G. Farben, Leverkusen; Nach Deutsche Hütte, Bremen (Krupp); Röschling Steel Works, Völklingen; and Vereinigte Aluminumwerke, A. G. Laute.

Recovery of Vanadium From Lead-Zinc Ores in Northern Rhodesia.—The production of vanadic oxide in the Broken Hill area of Northern Rhodesia was started in January 1930 (*19*). Minerals indigenous to this area that contain vanadium are descloizite and vanadinite, although others are present. Ore minerals with higher percentages of vanadium occur in oxidized fissures and cavities in dolomite.

Vanadium recovery in Northern Rhodesia has been a byproduct of lead and zinc production. According to the Mining Year Book (*113*), the Rhodesian Broken Hill Development Co., Ltd., has 300 claims on its Camarnor vanadium property in the Broken Hill district.

To provide power for operations, the company erected a hydroelectric powerplant utilizing the Mulungushi River. This plant began operating about 1925 and later was expanded. An additional powerplant on the Lunsemfwa River started operating in November 1945.

Vanadium production by the Rhodesian

Broken Hill Development Co. in Northern Rhodesia ceased in 1952. Before that time, production was small, although the country was one of the world's largest producers. Its output was exceeded only by that of the United States, South-West Africa, and Peru.

Like Peru, production gradually declined because supplies of higher grade ores became depleted. Presumably, facilities still exist for recovering concentrates and vanadium oxide.

Lateritic deposits, from which vanadium ores were mined (descloizite and vanadinite), resembled a brown clay and differed in V_2O_5 content. Gravity concentration was used exclusively for concentrating the vanadium minerals (*27*), as shown in figure 13.

Products made in the gravity concentration of vanadium ore were a 16.5-percent concentrate for shipping, also middlings and a slime concentrate containing 8.5 percent V_2O_5 for the production of fused oxide.

To produce fused vanadic oxide, as shown in figures 13, 14, and 15, the middlings and slime concentrate were ground to a minus 200-mesh, pumped to a mechanically agitated tank, and mixed with enough dilute sulfuric acid to give a solution containing 30 to 40 grams per liter of V_2O_5. The grinding operation introduced a small quantity of iron, which reduced the V_2O_5 to V_2O_4. It was necessary to oxidize the solution with manganese dioxide during leaching.

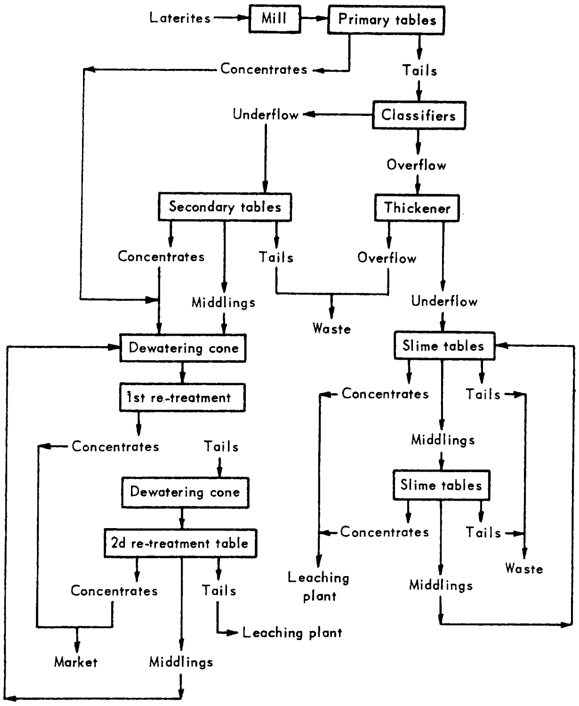

FIGURE 13.—Gravity Concentration of Vanadium-Bearing Ore at Rhodesian Broken Hill Development Co.

Sulfuric acid was added gradually. Cooling coils in the leaching tanks prevented the temperature from reaching 40° C., above which some vanadium might have precipitated in insoluble form. Leaching was continued until no more vanadium dissolved and resulted in a ratio of free acid to V_2O_5 of approximately 1:2. At this point in the process used at the Broken Hill plant, three possible methods were followed.

1. As shown in figure 14, the leach was settled and the clear solution decanted. Weak vanadium solution was added to the tanks, which were agitated and decanted. This procedure was repeated several times, depending upon the strength of the leach solution, the strength of the combined decants desired, and the allowable V_2O_5 content of the final solution to waste. The combined solution, which went to the next step, usually contained 15 grams V_2O_5 and 7 grams H_2SO_4. The combined decanted solution was filtered and sent to precipitate tanks, where it was heated to 90° C. After 4 hours at this temperature, precipitation of vanadic hydrate was almost complete. This precipitate was filtered and fused to oxide, which generally exceeded 91 percent V_2O_5. If copper or phosphorus were in excess of the allowable sales limit in the solution, the hydrate was purified before fusion (fig. 15). By dissolving it in caustic soda or soda ash, filtering it in a press, acidifying the filtrate, and precipitating the hydrate in the usual manner.

2. To prevent double precipitation, copper and phosphorus were removed by adding sodium sulfide or excess soda ash to the decanted solution before precipitation of the hydrate and after neutralization with zinc dross or lime. The precipitate was then filtered off, the solution acidified, and the hydrate precipitated.

3. In the third possible method used at the Broken Hill plant, the leach, which should contain 25 to 30 grams V_2O_5 and 12 to 15 grams H_2SO_4, was neutralized and treated with soda ash or sodium sulfide in the original tank, instead of being decanted. (See fig. 16.) The pulp was filtered, and the resulting filtrate was acidified. Reportedly, this procedure was followed only when tank capacity for the decantation method was not available.

If the lateritic-bearing vanadium ores contained much zinc silicate, which could contaminate the middlings and cause gels during leaching, the process was modified (fig. 14), to embody a preliminary silicate leach, tak-

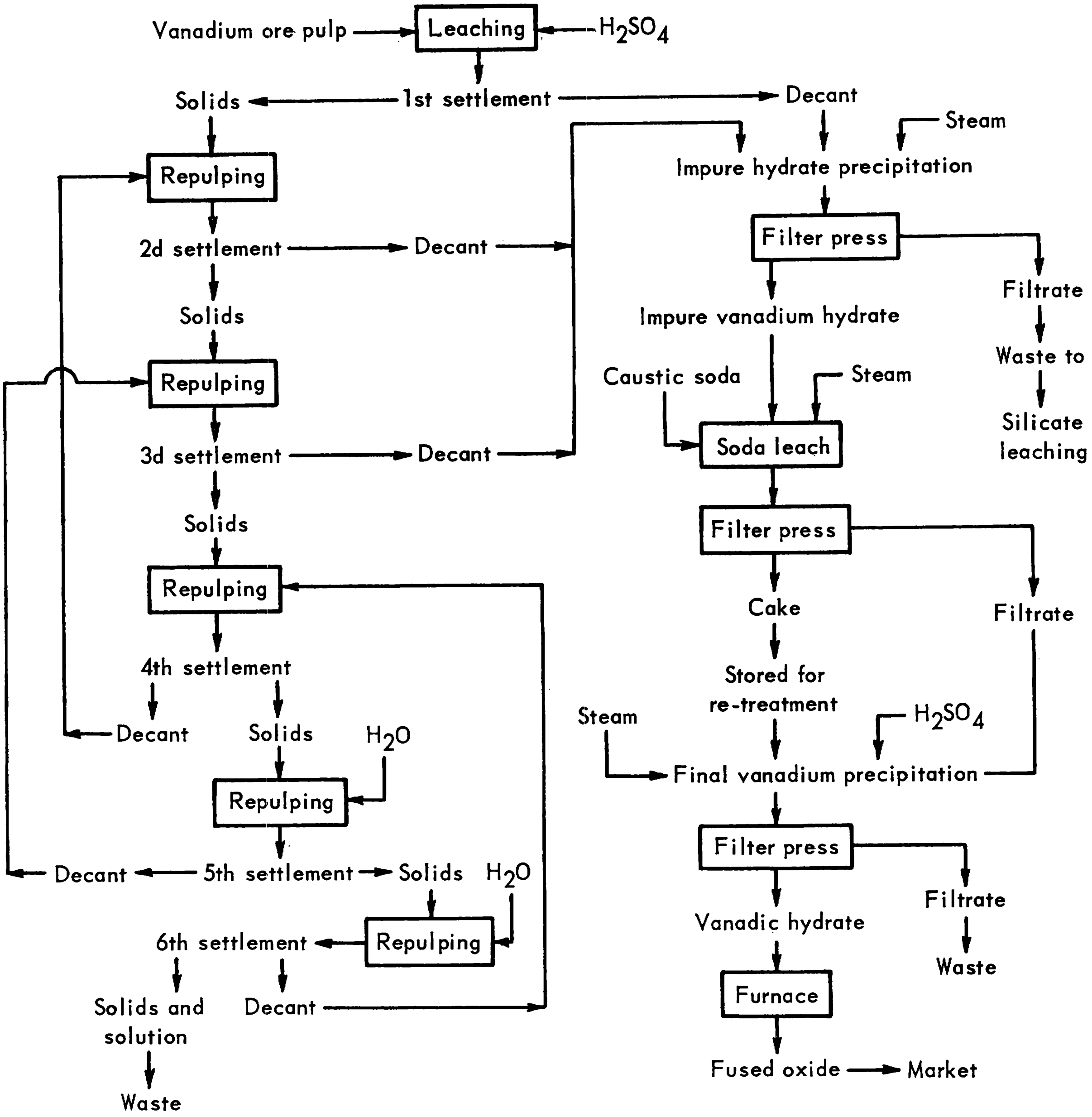

FIGURE 14.—Methods Used in Leaching Vanadium Concentrate at Rhodesian Broken Hill Development Co.

ing advantage of the comparatively low solubility of vanadium minerals in any but fairly concentrated acid solutions. The ore pulp was suspended in water or in the filtrate from the hydrate precipitation (to use its free acid content), and acid was added slowly to prevent free acidity. A leach could be obtained in which only zinc minerals, other than descloizite, dissolved. Settling and decantation, with one decanting wash, gave a material free from zinc silicates and suitable for vanadium leaching. Other extractive processes at the Broken Hill plant were concerned with the extraction of zinc, the electrolysis of zinc, and the rewetting and casting of the metal.

Recovery of Vanadium From Veta Madre Ore in Peru.—At the Jumasha reduction plant of Vanadium Corp. of America in Peru, the feed was Veta Madre ore, which consists of dark-green and dark-red altered shales containing replacements of calcium vanadates (*63*, p. 10).

The process for recovering vanadium from the ore was the subject of U.S. Patent 2,257-

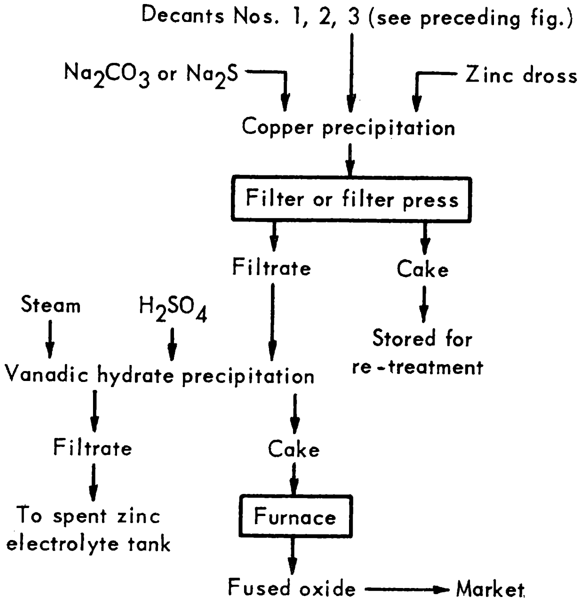

FIGURE 15.—Rhodesian Broken Hill Development Co. Method of Removing Copper and Phosphorus Before Precipitating Vanadium Hydrate.

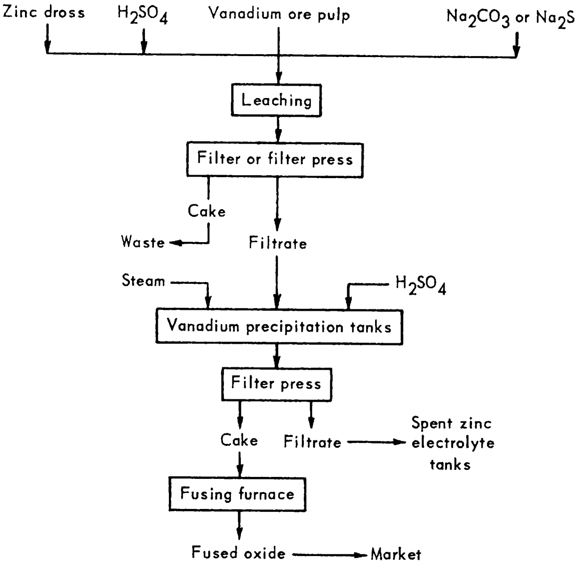

FIGURE 16.—Alternate Method Used at Broken Hill Plant to Remove Copper and Phosphorus Directly in Vanadium Leach Tank.

978 (*42*). A characteristic ore treated in accordance with the invention had the following composition:

	Percent
V	3.54
CaO	15.53
SO_3	25.91
Al_2O_3	11.18
SiO_2	24.44
Fe_2O_3	1.95

According to the patent, the process may be carried out as follows:

> The ore, crushed or comminuted to the desired fineness, say 20-mesh, is roasted in a suitable furnace at the desired temperature, usually between about 1,400° F. and 1,700° F., depending upon the type of ore or other material which is being treated. The roasted ore, while being maintained at or near the temperature of the roast, is quenched in water. The quenched ore is then ground to the desired degree of fineness with the water. The ground material is filtered, yielding a filtrate containing a large proportion of the vanadium originally contained in the ore, hereafter called "quench liquor," and a residue, hereafter called "quench residue." A leach of the quench residue is then made with a dilute sulfuric acid solution, say, a 4-percent solution; and the leached material is filtered, yielding a filtrate, hereafter called "acid liquor," containing an additional proportion of the vanadium contained in the ore and a final residue or tailing. The quench liquor and acid are then mixed; and, on being heated by suitable means and stirred meanwhile, a precipitate forms, usually considered to be V_2O_5. This precipitate is then filtered and washed according to common practice.

Figure 17 is a flowsheet illustrating the preferred manner of carrying out the process.

The precipitate, which averages about 65 percent V_2O_5, was shipped to Cambridge, Ohio, where it was converted from vanadium oxide to ferrovanadium.

PRODUCTION OF VANADIUM METAL

In 1927, J. W. Marden and M. N. Rich produced ductile vanadium metal experimentally (*79*, p. 5). They reacted vanadium pentoxide with calcium in the presence of calcium chloride, producing small globules of the metal. From the small quantity of the element made and fabricated into wire, certain physical and chemical properties of vanadium were ascertained. These small pieces of ductile vanadium wire were the only samples of vanadium available for many years.

Since 1927, many other researchers have attempted to produce ductile vanadium. E. D. Gregory reacted vanadium trioxide, which he obtained by hydrogen reduction of pentoxide, with calcium in the presence of calcium chloride to produce vanadium metal. The final product was a powder that could be worked by the usual procedures of powder metallurgy, taking into account the precautions necessary for a metal that reacts with nitrogen and oxygen and absorbs hydrogen.

Two scientists, R. K. McKechnie and A. U. Seybolt, in 1927 produced vanadium metal by similar techniques, except that they used iodine to increase the energy relationship. They reported that more than 0.07 percent

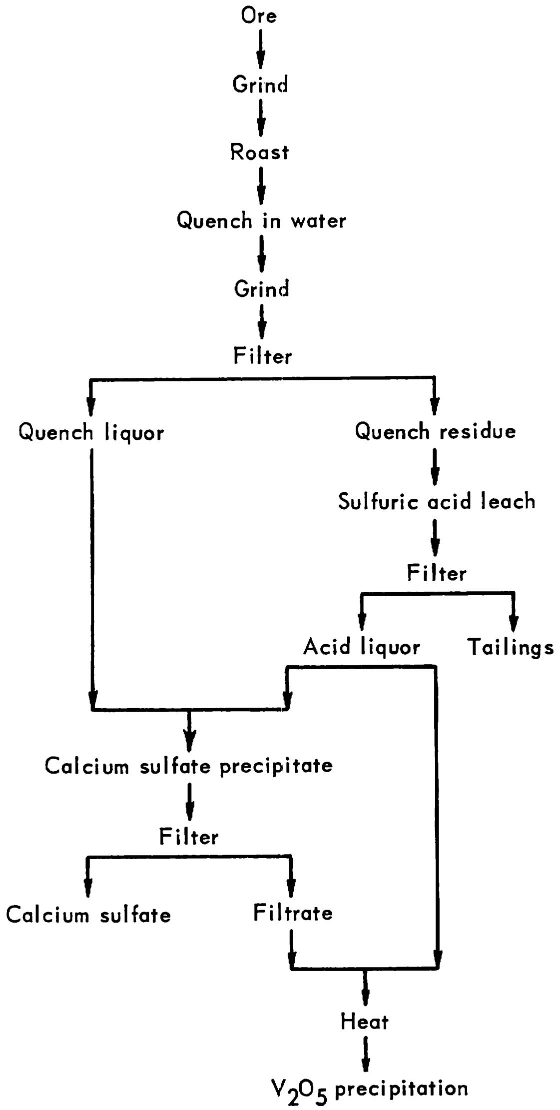

FIGURE 17.—Extraction of Vanadium Values From Vanadium Bearing Material, Mina Ragra, Peru.

oxygen and 0.028 percent nitrogen may cause brittleness.

A study of the reaction of vanadium with oxygen and nitrogen was made by E. A. Gulbransen and K. F. Andrew. They reported that vanadium reacts more readily with oxygen at 750° F. than does titanium but less rapidly than columbium, tantalum, and zirconium. According to these investigators, oxidation of vanadium increases rapidly with temperature, and vanadium reacts with nitrogen more readily than with the other metallic elements mentioned.

Massive vanadium metal is available commercially. The purity of metal, with advanced techniques, has continued to improve, but demand at present is limited pending development of uses. Vanadium metal (99.5 percent V) is now available as ingot, wire, rod, sheet, and tubings.

The most common method used in the United States to produce vanadium metal is the calcium reduction of the oxide—a method developed by McKechnie and Seybolt (*145*). In this method, moisture-free vanadium oxide of relative high purity, calcium metal, and iodine are charged into a heavy-walled steel bomb or cylinder, which is sealed tightly. With the application of heat, the reaction within the bomb soon produces a temperature and pressure sufficient to form a button or regulus of metal beneath the calcium oxide-calcium iodide slag. Vanadium metal produced by the reaction is removed from the enclosing cylinder after cooling and is cleaned of slag by leaching. Vanadium metal produced by the calcium reduction method analyzes about 99.7 percent vanadium and fractional percentages of oxygen, nitrogen, hydrogen, iron, and carbon.

Another commercial process developed by researchers of an English company, Magnesium Electron, Ltd., uses magnesium reduction of vanadium trichloride in an argon atmosphere at a temperature of 1,550° F. The reduction step is similar to the Kroll process used to produce titanium sponge. Vanadium trichloride is produced by chlorinating 80 percent ferrovanadium to vanadium tetrachloride and oxytrichloride. The vanadium tetrachloride is changed to trichloride by heating it under reflux in a stream of carrier gas. Upon completion of the reaction, any vanadium oxytrichloride that may have formed is removed by distillation.

The resulting vanadium sponge is separated from the magnesium chloride and excess magnesium by melting it under an argon atmosphere, heating it under a vacuum to 1,650° F., and finally leaching it. Vanadium metal produced by the magnesium reduction method analyzes about 99.7 percent vanadium and fractional percentages of oxygen, nitrogen, hydrogen, iron, and magnesium.

A vanadium metal analyzing over 90 percent V has been available commercially for several years. This metal is used for alloying and is made by an aluminothermic process. The oxygen content of the metal is high but can be lowered by increasing the aluminum content of the mix. Although the metal is not ductile, it is low in cost and suitable as melting stock for certain vanadium-base alloys. Industry is giving considerable attention to the development of a refining process to make metal of this type ductile at a reasonable cost.

The reguli resulting from the calcium and magnesium reduction methods are not suitable for either hot or cold working. Remelting of the reguli is required, and perhaps the most satisfactory remelting process is the vacuum-arc, consumable-electrode method. Remelting by this process removes the small quantities of oxygen and hydrogen and results in a more desirable, ductile metal. For small-scale work, vanadium buttons are cut into square bars and joined together to form an electrode, and for larger scale work the buttons are joined together to make a larger electrode. Vanadium sponge can be pressed into an electrode shape.

The vacuum induction method of remelting vanadium is feasible but difficult, because molten vanadium attacks most refractory materials and thus becomes contaminated. Only two refractories, beryllia and thoria, withstand molten vanadium or are relatively unreactive with it. The feasibility of coating crucibles with these refractories to lower costs may be practical but has not been investigated.

Nonconsumable, inert-atmosphere, arc melting of vanadium is used, but this method is not considered as desirable as the consumable-arc process.

Some of the highest purity vanadium metal is credited to a refining process developed by deBoer and Van Arkel. The cost of the metal is high because the starting material is high-purity vanadium metal. In the deBoer-Van Arkel process, vanadium tri-iodide is formed by reacting iodine vapor and vanadium metal in a heated and evacuated vessel. Within a quartz or pyrex chamber, a loop of vanadium wire is heated to incandescense. Vaporized vanadium iodide is decomposed into vanadium metal and iodine when it comes in contact with the hot wire. The metal deposits on the wire filament, causing it to grow in size. Refining vanadium metal by this method gives a product containing very minute qualities of objectional impurities, such as oxygen, nitrogen, and carbon. The final product is about 99.9 percent vanadium.

Because vanadium has been difficult to prepare and expensive, there has been little opportunity to use it in engineering materials. As the metal has two of the primary requisites for a material of construction, reasonable mechanical and chemical stability, it will undoubtedly have new applications (*79*, p. 9).

Some characteristics of vanadium that interest researchers are its resistance to aerated salt water, which is better than that of many stainless steels, and its resistance against dilute HCl and H_2SO_4, which is probably as good or better than that of most metals (*140*). However, vanadium corrodes readily in either dilute or concentrated nitric acid. (See table 2, p. 36.)

Vanadium and its alloys may be used in a weldable, formable, high-hot-strength sheet alloy for airframe service at temperatures up to 1,200° F.; as a fuel-element cladding for fast reactors in which interdiffusion, hot strength, and thermal conductivity are important; and as a diffusion barrier between steel and titanium in the manufacture of cladding between these metals.

FABRICATION TECHNIQUES

Massive vanadium is hot worked either with or without protective sheaths (*79*). Unsheathed masses of vanadium metal or ingots are conditioned by grinding or machining the surfaces before working. Subsequent rolling or extrusion without a sheathing necessitates working in a protective atmosphere. The sheathing technique is customary in small-scale industrial operations.

The common austenitic stainless steels are generally used for sheathing. The sheathing is fabricated by Heliarc welding into a box around the small vanadium ingots. Extra time is allowed for heating to insure a uniform temperature throughout the ingot. The initial optimum breakdown temperature is between 2,000° and 2,100° F., but once the ingot has been broken down the hot-working temperature usually ranges from 1,475° to 2,100° F. Some times, rolling may be carried on well below 1,475° F., with no work-hardening effects, and may be continued down to room temperature. From 1,100° to 1,300° F. is considered to be a good finishing range for the temperature. Subsequent to rolling, the protective sheath is removed and further prepared for processing by removing about one-sixteenth inch from the surface of the rolled article, but the need for removing surface metal depends upon the type of end product desired.

ROLLING

To make vanadium sheet or foil, the practice is to hot work the material down to about one-fourth inch thick. After this thickness is obtained, the sheet is cold rolled to produce the final article. To condition the sheet for cold rolling, the hot-worked material is annealed 1 hour at 1,650° F. in a vacuum or inert gas. After annealing, the surface hardness should be less than Rockwell B–85 to permit cold working. Greater hardness after annealing indicates insufficient surface removal of diffused material. Ductile vanadium worked at room temperature hardens very rapidly with initial deformation. With continued deformation, work hardening occurs less rapidly until maximum hardness is reached. Hardness of a very soft ingot may triple with as little as a 2-percent reduction in area, and the hardness may be near its maximum. The hardness of a harder ingot may be increased only a few numbers with a similar area reduction. Reductions in area up to 85 percent may be attained without intermediate annealing, but the Rockwell hardness may reach B–90 to B–100. If the surface hardness exceeds Rockwell B–95, edge cracking probably will occur.

Simple bars and sheet may be cold rolled at room temperature, and as vanadium does not oxidize below 575° F. other shapes of the metal can be cold rolled between 400° and 600° F.

Vanadium metal has been found to be free cutting, and its machinability is similar to that of cold-rolled steel. It is easier to machine than nickel, titanium, and stainless steel but not as easy to machine as aluminum and copper.

WELDING AND FORMING

Pure, ductile vanadium metal has smooth welding characteristics. It may be welded by a Heliarc torch with adequate argon shielding.

Because vanadium has good workability at mildly elevated temperatures, it may be formed in the usual manner by bending, pressing, and stamping.

PRODUCTION OF FERROVANADIUM

Vanadium in ores, slags, or chemically produced compounds, such as technical grade V_2O_5, can be reduced by using carbon, silicon, or aluminum. The methods and reductants used to produce ferrovanadium are determined by the grade desired. The end products or grades of ferrovanadium are based on the vanadium content and the amounts of carbon, silicon, and aluminum in the residue from the reduction process.

Carbon is the least expensive reducing agent, but it is difficult to regulate its content in the end product. Therefore, reduction with this agent is probably obsolete. Moreover, undesirable secondary reactions of carbon and vanadium involve the partial reduction of vanadium to lower oxides of higher melting points. If not avoided, these reactions lower yields. Successful production of ferrovanadium requires heating the arc-furnace charge to the correct operating temperature and regulating it so that reduction of the pentoxide proceeds directly to the metallic stage without formation of lower oxides. Confining the reduction to a narrow zone with a high energy input prevents the formation of intermediate compounds. Reduced metal, as droplets, descends rapidly through the surrounding slag and unreacted charge to the metal pool at the bottom of the furnace.

The best arc furnaces for producing ferrovanadium are designed with a deep hearth; a narrow, rectangular cross section; and a water-cooled roof with electrode openings. A 4,000-kilowatt furnace has a power input of 190 kilowatts per square foot of hearth area. Furnace electrodes are arranged in line and create a high-energy reduction zone where they dip through the charge into the slag. A well-mixed charge consisting of small sized particles of V_2O_5, coke, steel scrap, and fluxes is fed into the reduction zone automatically. Tapping of metal and slag in this process is intermittent and separate.

Ferrovanadium of low carbon content can be made by reducing V_2O_5 with ferrosilicon. Because silicon is not a powerful reducer of vanadium oxides, a two-stage process is required. In this method, a charge of pentoxide, 90-percent ferrosilicon, lime, and fluorspar is smelted in an electric furnace lined with magnesite. The primary metal produced in the first step contains about 30 percent vanadium and the slag, 0.4 to 0.9 percent vanadium. In the second step, the primary metal is refined with V_2O_5 and lime. The secondary slag is returned as part of the charge to produce primary metal.

A high-silicon, low-carbon vanadium-silicon alloy may also be produced by smelting V_2O_5, silica, coke, and fluxes. After the primary alloy has been ground and mixed with V_2O_5 the mixture is reacted to produce ferrovanadium. Operations are usually performed in an electric furnace that requires considerable unit expenditure of power.

Although aluminum is generally a more expensive reducing agent, the process is exothermic, yields are good, and the product is relatively pure and has a high vanadium content. The 50-percent grades of ferrovanadium are generally produced in a standard, open-top, three-phase electric-arc furnace lined with magnesia. A charge consists of V_2O_5, aluminum, iron scrap, and fluxes such as calcium fluoride.

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[9] Reprinted with permission of William Rostoker (*144*).

The electric furnace is required only to kindle the reaction by generating a threshold temperature of 1,730°±28° F. and at later stages to superheat the slag to improve the yield. The temperature of the reaction is controlled by adjusting the particle size of the reagents and the rate of feeding the charge; by working with partly prereduced material; or by replacing part of the aluminum with a less active reducing agent, such as calcium carbide, silicon, or carbon. Slag is decanted from the furnace. Later, the metal is poured through the slag; this step serves to clean the metal and remove additional values from the slag. Efficiency of the process improves with the volume of the operation.

The 70- to 80-percent grades of ferrovanadium are produced in magnesite-lined pots, which are ignited by a charge containing barium dioxide and aluminum to develop kindling temperature of 1,730° F.

CHAPTER 6. SUPPLY AND DISTRIBUTION

UNITED STATES

PRODUCTION

In the United States, the center of vanadium-ore mining is the Colorado Plateau in southwestern Colorado and southeastern Utah, with extensions into northern Arizona and northern New Mexico. Vanadium production in these States is a byproduct or coproduct of uranium mining and milling.

Colorado has been the largest vanadium ore producing State for many years. Utah and Arizona are the only other major vanadium ore producing States; however, New Mexico has been a small, consistant producer of ore from which vanadium has been recovered. In addition, small quantities of vanadium have been extracted from ores produced in South Dakota, Montana, Wyoming, and California. Before 1955, vanadium was also recovered as a byproduct of phosphate rock mining and milling. Table 15 shows the vanadium in ores and recoverable vanadium [10] produced domestically, 1932 to 1959, inclusive.

A yearly canvass is conducted on receipts, disposition, and stocks of vanadium ore and on production, receipts, shipments, and stocks of vanadium oxide.

TABLE 15.—*Vanadium and recoverable vanadium in ore and concentrate produced in the United States, 1930–59, in short tons*

Year	Production of vanadium [1] in ores (mine products)	Recoverable vanadium in ores	Year	Production of vanadium [1] in ores (mine products)	Recoverable vanadium in ores
1930	(3)	(3)	1945	1,482	(3)
1931	(3)	(3)	1946	636	510
1932	270	(3)	1947	1,059	821
1933	2	(3)	1948	894	670
1934	[2] 6	(3)	1949	1,580	1,188
1935	[2] 25	(3)	1950	2,298	1,598
1936	70	(3)	1951	3,040	2,126
1937	543	(3)	1952	3,588	2,571
1938	807	(3)	1953	4,643	3,057
1939	992	(3)	1954	4,930	3,026
1940	1,081	(3)	1955	4,983	3,286
1941	1,257	(3)	1956	5,635	3,868
1942	2,220	(3)	1957	7,294	3,691
1943	2,793	(3)	1958	7,266	3,030
1944	1,764	(3)	1959	7,392	3,719

[1] Measured by receipts at mills.
[2] Carnotite ores only.
[3] Data not available.

In addition, a monthly canvass, begun in January 1956, is conducted on the domestic consumption of and foreign trade in vanadium. This canvass is a continuation and modification of a quarterly canvass which was discontinued in 1947. The monthly report contains information on stocks held at consumers' plants, consumption of vanadium by form, consumption by end uses, and current data on exports and imports.

Table 16 gives production of recoverable vanadium in ore and concentrate for Colorado, Utah, and other States. Like mine production of vanadium, the recoverable vanadium in ores and concentrates has generally increased yearly as greater tonnages were produced. Many uranium mills do not recover vanadium, but vanadium-bearing tailings at some mills are impounded for possible future use.

In 1957, vanadium recovery units were operated in Colorado by Climax Uranium Corp., Grand Junction; Union Carbide Nuclear Co. (formerly United States Vanadium Co.), at Rifle and Uravan; and Vanadium Corp. of America, at Durango and Naturita. Some vanadium was also recovered in 1957 at the Kerr-McGee Industries, Inc., mill at Shiprock, N.M. In 1958, only three mills, at Grand Junction, Durango, and Uravan, Colo., produced vanadium pentoxide. Mills recovering vanadium in 1959 were operated by

TABLE 16.—*Recoverable vanadium in ore and concentrate produced in the United States, 1946–59, by States*

(Short tons of contained vanadium)

State	1946	1947	1948	1949	1950	1951	1952
Colorado	402	627	384	873	1,119	1,584	2,099
Utah	23	16	34	76	141	191	97
Arizona and other States [1]	85	178	252	239	338	351	375
Total	510	821	670	1,188	1,598	2,126	2,571

State	1953	1954	1955	1956	1957	1958	1959
Colorado	2,265	2,264	2,298	2,791	3,132	2,395	2,949
Utah	192	288	498	549	508	376	536
Arizona and other States [1]	600	474	490	527	51	259	234
Total	3,057	3,026	3,286	3,867	3,691	3,030	3,719

[1] Includes Idaho, 1946–54; Montana, 1957; New Mexico, 1947–48, 1950–54, 1956–59; South Dakota, 1954; and Wyoming, 1954, 1956–58.

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[10] Recoverable vanadium represents the vanadium that can be recovered from ores produced but not necessarily processed and is based upon the general recovery rate for mills producing vanadium pentoxide during a specific year.

Climax Uranium Corp., Grand Junction, Colo.; Union Carbide Nuclear Co., at Rifle and Uravan, Colo.; and Vanadium Corp. of America, at Durango, Colo.

The vanadium recovery rate at mills producing vanadium pentoxide varies yearly, depending upon demand. Curtailment of the AEC buying program and poorer grades of vanadium-bearing ore may have been responsible for the decline in 1958.

The first step in the processing of domestic vanadium-bearing ore to a marketable form is the separation and conversion of the vanadium to vanadium pentoxide. This product usually contains 85 to 92 percent V_2O_5 and is the raw material for manufacturing ferrovanadium and other vanadium products. Table 17 gives quoted prices for vanadium-bearing raw materials and products. A high-purity vanadium pentoxide, which contains about 99.5 percent V_2O_5, is available commercially.

Production of vanadium pentoxide increased from 1946 to 1956 under the stimuli of wartime conditions, postwar industrial expansion, and increased foreign demand. Reflecting the economic recession in 1957 and 1958, production of vanadium pentoxide declined. Increased foreign production, resulting in a decrease in exports, plus a decline in domestic iron and steel production, poorer grade ore, and curtailment of the AEC vanadium purchasing program were probably contributory factors to the decrease in production in 1957 and 1958. In 1959, production of vanadium pentoxide again increased. Owing to the domestic steel strike in 1959 and increased steel production in Europe, exports of vanadium-bearing materials doubled in 1959. Table 18 gives vanadium pentoxide production from 1946 to 1959, including oxide produced from foreign chrome ores and as a byproduct of domestic phosphate rock mining and milling (1948–54) and Peruvian concentrates before 1956.

TABLE 17.—*Quoted prices of vanadium raw materials and products*[1]

Year	Ore [2]	Vanadium oxide [3]	Ferrovanadium [4]	Vanadium metal	High-Purity vanadium metal
1940..	$0.27½	$1.10	$2.70–$2.90	....	....
1941..	.27½	1.10	2.70– 2.90	....	....
1942..	.27½	1.10	2.70– 2.90	....	....
1943..	.27½	1.10	2.70– 2.90	....	....
1944..	.27½	1.10	2.70– 2.90	....	....
1945..	.27½	1.10	[5] 2.70– 2.90	....	....
			2.75– 2.90	....	....
1946..	.27½	1.10	[6] 2.75– 2.90	....	....
			2.70– 2.90	....	....
1947..	.27½	$1.10– 1.20	2.70– 2.90	....	....
			[7] 2.90– 3.10	....	....
1948..	.27½	1.20	2.90– 3.10	....	....
1949..	.27½	1.20	2.90– 3.10	....	....
		[8] 1.00– 1.06			
1950..	.27½	1.00– 1.06	2.90– 3.10	....	....
			[9] 3.05– 3.25	....	....
			[10] 3.00– 3.25	....	....
1951..	.27½	1.00– 1.06	$3.00– 3.10– 3.20	....	....
	[11] .31	[12] 1.28– 1.34	3.00– 3.10– 3.30	....	....
1952..	.31	1.28– 1.33	3.00– 3.10– 3.20	....	....
1953..	.31	1.28– 1.33	3.00– 3.10– 3.20	....	....
1954..	.31	1.28– 1.33	3.00– 3.10– 3.20	....	....
1955..	.31	1.28– 1.33	[13] 3.00– 3.10– 3.20	$3.45	....
			3.10– 3.20– 3.30	....	....
1956..	.31	1.28– 1.33	[14] 3.10– 3.20– 3.30	$3.45	....
			3.20– 3.30– 3.40		
1957..	.31	1.28– 1.38	3.20– 3.30– 3.40	[15] $3.45–3.65	$40.00
1958..	.31	1.28– 1.38	3.20– 3.30– 3.40	3.65	40.00
1959..	.31	1.38	3.20– 3.30– 3.40	3.45–3.65	40.00

[1] Engineering and Mining Journal; Oil, Paint and Drug Reporter—contract prices.

[2] Cents per pound of contained V_2O_5, f.o.b. mine.

[3] Technical grade, containing 88 to 92 percent V_2O_5. Price based on V_2O_5 content per pound.

[4] Per pound of contained vanadium, depending upon grade. From 1951 to 1958, prices indicate open-hearth, crucible, or high-speed grade.

[5] Price change Mar. 1.

[6] Price change Dec. 19.

[7] Price change September.

[8] Price change June 23.

[9] Price change Nov. 9.

[10] Price change Nov. 23.

[11] Price change March.

[12] Price change Sept. 22.

[13] Price change Feb. 15.

[14] Price change Sept. 20.

[15] Price change July 11.

Two companies, Union Carbide Metals Co. and Vanadium Corp. of America, are the principal producers of ferrovanadium in the United States. Data regarding production of this commodity are not available because of the limited number of producers.

TABLE 18.—*Production of vanadium pentoxide in the United States, 1946–59, in short tons* [1]

Year	Gross weight	V_2O_5 content	Year	Gross weight	V_2O_5 content
1946......	1,493	1,316	1953.....	5,070	4,475
1947......	3,073	2,733	1954.....	6,368	5,628
1948......	2,198	1,949	1955.....	7,426	6,552
1949......	2,043	1,798	1956.....	7,963	7,030
1950......	3,669	3,250	1957.....	7,224	6,449
1951......	4,470	3,972	1958.....	5,470	4,983
1952......	4,355	3,864	1959.....	7,906	7,305

[1] Includes a relatively small quantity recovered as a byproduct of Peruvian concentrate and foreign chromite ore.

FOREIGN TRADE

Table 19 gives data on vanadium ore and concentrate, vanadium-bearing flue dust, and ferrovanadium imported for consumption in the United States from 1930 to 1959. From 1952 to 1955, there was a marked decline in imports of ore and concentrate (vanadium content) from Peru. In 1956, imports stopped completely. This decline and cessation of Peruvian imports was the result of depletion of better grades of ore, which made it economically difficult for Peruvian concentrate to compete with the byproduct vanadium recovered from uranium production of the Colorado Plateau.

The United States has been producing vanadium in excess of requirements. Part of the excess production has been exported to free world nations deficient in supplies of vanadium. Data on exports of vanadium from the United States from 1941 to 1959 by classes are given in table 20. Table 21 shows the countries that were the main foreign recipients of U.S. exports in 1958 and 1959.

CONSUMPTION

In 1955, for the first time, data on the consumption of vanadium were collected and published by the Bureau of Mines. Data for 1955–59, shown in table 22, indicate that ferrovanadium was the major item of consumption. Smaller quantities were consumed as oxides; ammonium metavanadate; and "other" forms such as vanadium metal, aluminum-vanadium alloys, vanadium-titanium pig iron, vanadium briquettes, vanadium-bearing scrap, and cobalt-vanadium.

Ultimate consumption of vanadium is shown in table 23. The largest use of vanadium was as ferrovanadium in the manufacture of high-speed steel and other alloy steels, including engineering steel, high-strength structural steel, and wear-resistant cast iron.

Some vanadium was used in making nonferrous alloys, such as titanium-vanadium and aluminum-vanadium.

Not revealed under the "Other" category in table 23 are many minor uses of vanadium, such as coatings for welding rods and electrodes, in high-temperature alloys, in heat-resistant stainless steel, in carbon steel and ingots, a deoxidizer for carbon steel, in ceramics and ceramic pigments, in manufacturing arc lighting carbons, for hard facing products, in glass manufacture, a bleaching agent in processing color film, in magnet alloys, in ordnance material, a trace element in agronomy field tests, in catalysts, and for research purposes.

FREE WORLD NATIONS

PRODUCTION

World production of vanadium ore and concentrate has been limited to a few nations, including the United States, Finland, South-West Africa, Peru, Northern Rhodesia, and Angola.

Finland is a new source of vanadium in Western Europe. Commercial extraction of vanadium pentoxide from titaniferous magnetites was begun in 1956. Data on production for 1956–59 are shown in table 24. Con-

TABLE 19.—*Vanadium ore and concentrate, vanadium-bearing flue dust, and ferrovanadium imported for consumption in the United States, 1930–59*

[Bureau of the Census]

Year	Vanadium ore and concentrate,[1] short tons			Vanadium-bearing flue dust, short tons			Ferrovanadium	
	Gross weight	Vanadium content	Value	Gross weight	Vanadium content	Value	Short tons (gross weight)	Value
1930	5,788	(2)	$491,633	(2)	(2)	(2)	(2)	(2)
1931	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
1932	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
1933	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
1934	1,754	207	145,506	(2)	(2)	(2)	(2)	(2)
1935	476	47	40,070	(2)	(2)	(2)	(2)	(2)
1936	1,867	171	155,730	(2)	(2)	(2)	(2)	(2)
1937	7,403	629	638,799	(2)	(2)	(2)	(2)	(2)
1938	9,981	692	891,475	(2)	(2)	(2)	(2)	(2)
1939	15,694	1,066	991,511	(2)	(2)	(2)	(2)	(2)
1940	22,551	1,287	1,216,705	(2)	(2)	(2)	(2)	(2)
1941	12,323	1,069	1,012,991	(2)	(2)	(2)	(2)	(2)
1942	18,246	1,211	1,274,483	312	77	$29,545	(2)	(2)
1943	11,059	1,026	1,080,150	374	32	53,553	(2)	(2)
1944	2,124	642	633,719	96	20	28,059	(2)	(2)
1945	4,388	775	725,362	67	13	19,378	(2)	(2)
1946	1,392	396	390,077	49	10	13,480	(2)	(2)
1947	1,637	492	448,076	72	36	15,483	(2)	(2)
1948	2,017	526	534,374	...	...	...	(2)	(2)
1949	1,014	276	272,124	...	...	...	(2)	(2)
1950	2,555	729	708,806	5	(4)	2,475	65	$91,193
1951	1,947	491	526,941	...	...	...	62	100,261
1952	2,169	522	599,203	6	(4)	2,425	11	22,132
1953	1,480	358	421,091	5	(4)	2,237	9	12,584
1954	592	198	238,222	...	...	...	...	...
1955	[3] 291	[3] 92	[3] 104,230	...	...	...	...	...
1956	...	...	...	...	...	...	...	...
1957	...	...	...	...	...	...	...	...
1958	...	...	...	...	...	...	...	...
1959	5	3	9,618	...	...	...	16	38,598

[1] Figures for 1945–52 probably also included fused vanadium oxide.

[2] Not separately recorded.

[3] Includes 46 short tons of concentrate containing 15 short tons of vanadium valued at $16,811, received but not reported by the U.S. Department of Commerce.

[4] Less than 1 ton.

TABLE 20.—*Exports of vanadium from the United States, 1930–59 by classes*

[Bureau of the Census]

Year	Vanadium ore, concentrates, vanadic oxide, vanadium oxide, and vandates (except chemically pure grades) [1]		Ferrovanadium and other vanadium alloying materials containing over 6 percent vanadium		Vanadium metal, alloys, and scrap		Vanadium-bearing flue dust and other waste materials	
	Short tons (vanadium content)	Value	Short tons (gross weight)	Value	Short tons (gross weight)	Value	Short tons (vanadium content)	Value
1930–40	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
1941	13	$63,213	(2)	(2)	(2)	(2)	(2)	(2)
1942	11	86,218	(2)	(2)	(2)	(2)	(2)	(2)
1943	19	(2)	222	$518,322	(2)	(2)	(2)	(2)
1944	3	(2)	596	2,212,490	(2)	(2)	(2)	(2)
1945	57	(2)	(2)	(2)	(2)	(2)	(2)	(2)
1946	3	40,541	57	161,289	(2)	(2)	(2)	(2)
1947	4	15,788	89	266,040	(2)	(2)	(2)	(2)
1948	7	32,263	119	390,428	1	$11,308	(2)	(2)
1949	7	26,266	97	350,558	1	17,851	(2)	(2)
1950	(3)	2,615	41	183,307	2	2,688	(2)	(2)
1951	1	6,581	61	190,346	1	6,481	(2)	(2)
1952	60	280,216	147	529,360	51	12,862	(2)	(2)
1953	6	32,141	78	296,157	(2)	(2)	27	$31,285
1954	21	120,311	70	237,333	(2)	(2)	12	13,609
1955	865	3,768,358	220	991,955	(2)	(2)	43	66,472
1956	928	4,046,100	139	650,955	(2)	(2)	14	27,185
1957	500	2,114,700	134	519,955	(2)	(2)	58	118,894
1958	631	2,624,960	76	294,933	(2)	(2)	6	2,100
1959	1,240	4,667,764	152	529,697	(2)	(2)	42	40,317

[1] Classed as ores and concentrates but probably also includes fused vanadium pentoxide and flue dust when not listed.
[2] Not separately classified except for years given.
[3] Less than 1 ton.

templated production of 600 to 1,000 tons of vanadium pentoxide per year would make Finland one of the free world's largest producers.

Production of vanadium in South-West Africa was relatively consistant from 1951 to 1955, declined from 1956 to 1958, and rose again in 1959.

Vanadium production in Peru declined from 1948 to 1954 owing to depletion of better grade ore deposits and economic competition with coproduct uranium-vanadium production in the United States. Mining and milling operations were suspended late in 1954. Exports from Peru in 1955 consisted of a small stockpile of material remaining at the mill after operations ceased and were shipped to the United States for consumption.

Production of vanadium ore in Northern Rhodesia was terminated in 1952 owing to depletion of suitable ores.

Argentina is believed to produce some vanadium-bearing ore from widely scattered deposits in the Provinces of Cordoba, Mendoza, and San Luis.

In 1956, Angola, a Portuguese colony in South-West Africa, produced ores containing 11 tons of vanadium. Production was continued in 1957, 1958, and 1959, but quantities were small.

Production of vanadium was started in the Transvaal, Union of South Africa, in September 1957. If preliminary estimates are correct, the Transvaal could become one of the larger free-world producers of vanadium providing economic conditions are favorable.

FOREIGN TRADE

Information is lacking on total imports of vanadium-bearing materials into free-world nations. Some of the imports of many free-world nations come from the United States, as indicated by the exports (tables 22 and 23) from this country. Imports to Western European nations are also derived from South-West Africa, Finland, and the Transvaal.

The United States was the primary recipient of vanadium concentrate produced in Peru until production was stopped late in 1955. Vanadium produced in South-West Africa, the Transvaal (Union of South Africa), and Finland is exported primarily to countries of northern Europe.

CONSUMPTION

Data on consumption of vanadium-bearing materials and end uses of vanadium products are not available for nations outside the United States. Exports from the United States to free-world nations (table 23) indicate that the major vanadium-bearing materials imported by these nations for the production of vanadium-bearing products include vanadium pentoxide,[11] ferrovanadium

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[11] Included in the same Bureau of the Census classification are ores and concentrate, vanadic oxide, vanadium oxide, and vanadates.

and other alloying materials, and vanadium-bearing flue dust and other waste materials.

SOVIET BLOC

PRODUCTION AND CONSUMPTION

Information is not available on either the production or consumption of vanadium in nations comprising the Soviet bloc.

TABLE 21.—*Exports of vanadium from the United States, 1958–59, by countries, in short tons*

[Bureau of the Census]

Country	Ferrovanadium and other vanadium alloying materials containing over 6 percent vanadium (gross weight)		Vanadium ore, concentrates, pentoxide, vanadic oxide, vanadium oxide, and vanadates, except chemically pure grade (vanadium content)		Vanadium flue dust and other vanadium waste materials (vanadium content)	
	1958	1959	1958	1959	1958	1959
North America:						
Canada	63	151	4	6	......	......
Mexico	......	......	2	1	......	......
Total	63	151	[1] 7	[1] 8	......	......
South America:						
Argentina	......	......	......	1	......	......
Brazil	......	(2)	1	2	......	......
Venezuela	(2)	(2)	......	......	......	......
Total	(2)	1	1	[1] 4	......	......
Europe:						
Austria	......	......	323	782	......	......
Belgium-Luxembourg	......	......	12	(2)	......	......
France	......	......	97	108	......	......
Germany, West	11	......	9	3	......	......
Italy	......	......	27	25	......	......
Netherlands	......	......	46	43	6	39
Sweden	1	......	......	17	......	......
Trieste	......	......	9	84	......	......
United Kingdom	(2)	......	(2)	(2)	......	......
Total	[1] 13	......	[1] 524	[1] 1,063	6	39
Asia:						
India	......	......	(2)	(2)	......	......
Japan	(2)	......	99	165	......	2
Total	(2)	......	99	[1] 166	......	2
Grand total:						
Short tons	76	152	631	[1] 1,240	6	[1] 42
Value	$294,933	$529,697	$2,624,960	$4,667,764	$2,100	$10,317

[1] Figures do not add to totals because of the rounding of numbers.
[2] Less than 1 ton.

TABLE 22.—*Vanadium consumed in the United States, 1955–59, by forms*[1]

(Short tons of contained vanadium)

Form	1955		1956		1957		1958		1959	
	Consumption	Percent of total	Consumption	Percent of total	Consumption	Percent of total	Consumption	Percent of total	Consumption	Percent of total
Ferrovanadium	1,453	85	1,527	77	1,374	77	1,022	81	1,492	79
Oxide	128	8	129	7	132	7	69	6	152	8
Ammonium metavanadate	67	4	84	4	100	6	88	7	112	6
Other	52	3	248	12	184	10	80	6	135	7
Total	1,700	100	1,988	100	1,790	100	1,259	100	1,891	100

[1] Figures are believed to represent about 90 percent of total consumption.

TABLE 23.—*Vanadium consumed in the United States, 1955–59, by uses*[1]

(Short tons of contained vanadium)

Use	1955		1956		1957		1958		1959	
	Consumption	Percent of total	Consumption	Percent of total	Consumption	Percent of total	Consumption	Percent of total	Consumption	Percent of total
High-speed steel..................	514	30	443	22	395	22	194	15	412	22
Other alloy steel..............	972	57	1,109	56	1,023	57	845	67	1,153	61
Alloy cast iron...............	28	1	29	1	24	1	19	2	25	1
Nonferrous alloys............	61	4	261	13	184	10	78	6	121	6
Chemicals..................	81	5	91	5	103	6	68	6	135	7
Other........................	44	3	55	3	61	4	55	4	45	3
Total.	1,700	100	1,988	100	1,790	100	1,259	100	1,891	100

[1] Figures are believed to represent about 90 percent of total consumption.

TABLE 24.—*World production of vanadium in ores and concentrates, 1930–58, in short tons*

[Compiled by Pearl J. Thompson and Berenice B. Mitchell]

Year	World total[1]	North America		South America		Europe, Finland	Africa			
		United States	Mexico	Argentina	Peru		Angola	Northern Rhodesia	South-West Africa	Union of South Africa
1930...........	1,678	[2] 584	....	....	528	....	....	62	504	....
1931...........	1,710	[2] 981	....	....	....	....	....	238	491	....
1932...........	944	270	....	....	....	....	....	338	336	....
1933...........	62	2	....	....	....	....	....	40	20	....
1934...........	130	[2] 6	....	....	[3] 83	....	....	3	37	....
1935...........	484	[2] 25	....	....	74	....	....	191	194	....
1936...........	1,074	69	....	....	177	....	....	225	603	....
1937...........	2,153	543	50	....	650	....	....	259	651	....
1938...........	2,855	[4] 807	111	....	911	....	....	412	614	....
1939...........	3,207	[4] 992	88	17	1,120	....	....	423	567	....
1940...........	3,298	[4] 1,045	35	1	1,339	....	....	406	472	....
1941...........	3,059	[4] 1,257	(5)	7	1,121	....	....	377	297	....
1942...........	4,260	[4] 2,220	....	....	1,113	....	....	428	499	....
1943...........	4,833	[4] 2,793	....	....	934	....	....	470	636	....
1944...........	3,039	[4] 1,764	....	4	567	....	....	280	424	....
1945...........	2,947	[4] 1,482	....	3	758	....	....	241	463	....
1946...........	1,421	[6] 510	....	7	355	....	....	75	474	....
1947...........	1,682	[6] 821	....	8	480	....	....	62	311	....
1948...........	1,630	[6] 670	....	(5)	563	....	....	191	206	....
1949...........	2,040	[6] 1,188	....	(5)	503	....	....	169	130	....
1950...........	2,405	[6] 1,598	....	1	481	....	....	....	325	....
1951...........	3,300	[6] 2,126	....	(5)	495	....	....	93	533	....
1952...........	3,788	[6] 2,571	....	(5)	482	....	....	47	638	....
1953...........	4,002	[6] 3,057	....	(5)	349	....	....	....	593	....
1954...........	3,868	[6] 3,026	....	(5)	209	....	....	....	633	....
1955...........	3,996	3,286	....	....	78	....	....	....	632	....
1956...........	4,230	3,868	....	(5)	....	43	11	....	303	....
1957...........	4,295	3,691	....	(5)	....	290	1	....	305	8
1958...........	4,231	3,030	....	(5)	....	430	20	....	435	316
1959...........	5,325	3,719	....	(5)	....	[7] 557	[8] 11	....	719	319

[1] Total represents data only for countries shown and excludes vanadium in ores produced in Belgian Congo, Morocco (Southern Zone), Norway, Spain, and U.S.S.R., for which figures are not available.

[2] Estimated data from Weltmontanstatistik, 1927–37, Stuttgart.

[3] Shipments from stock.

[4] Mine shipments.

[5] Negligible.

[6] Includes vanadium recovered as a byproduct of phosphate-rock mining, 1946–54.

[7] Exports.

[8] Estimate.

CHAPTER 7. STRUCTURE OF THE VANADIUM INDUSTRY

UNITED STATES

MINING

The uranium-vanadium mining industry expanded rapidly after 1948. At that time, many small operators worked deposits containing lenses or pods of carnotite ore which seldom extended far from the surface and were easily and quickly retrieved. Since 1948, ore deposits discovered at greater depths have resulted in more complex mines and mining methods. The shaft type of mine, with more expensive equipment and ventilating systems, is common throughout the Colorado Plateau. Conversely, large ore deposits have been found near the surface. In the Grants area, New Mexico, an open-pit mine is a major source of uranium-vanadium ore. However, the vanadium content of the ore is low, and vanadium is not known to be retrieved (1959) with the uranium at mills.

Most of the vanadium produced domestically comes from several hundred uranium-vanadium mines scattered widely throughout the Colorado Plateau. A small part of the domestic output of vanadium is recovered from imported chromite ores.

ORE BUYING STATIONS AND MILLS

Producers of uranium-vanadium ore formerly delivered their product to an AEC or an authorized private ore-buying station. Payments of U_3O_8 in ores was governed by regulations set forth periodically by the AEC. The AEC, on a contract basis with certain mills, paid for the V_2O_5 content of ore, as stipulated in Domestic Uranium Circular 5, amended October 9, 1953. The price paid for the V_2O_5 content of ores, as given in this circular, was 31 cents per pound. In 1958–59, Lucius Pitkins, Inc., operated the only ore-buying station for the Government. This ore buying station was located at the Government-owned mill at Monticello, Utah, operated by National Lead Co. Uranium-vanadium ore buying stations operating in 1957 included:

Operator:	*Location*
Climax Uranium Co.	Grand Junction, Colo.
Kerr-McGee Oil Industries, Inc.	Shiprock, N. Mex.
Union Carbide Nuclear Co.	Rifle, Colo. Uravan, Colo. Slick Rock, Colo. Greenriver, Utah. Thompsons, Utah.
Vanadium Corp. of America.	Durango, Colo. Naturita, Colo.
Vitro Uranium Co.	Salt Lake City, Utah.
Rare Metals Corp. of America.	Riverton, Wyo.
Mines Development, Inc.	Edgemont, S. Dak.
Lucius Pitkin, Inc.	Bluewater (Grants), N. Mex. Globe, Ariz. Marysvale, Utah. Moab, Utah. Monticello, Utah. Tuba City, Ariz. White Canyon, Utah.

Of the ore-buying stations and mills operating in 1957, only the Union Carbide Nuclear Co. mills at Rifle and Uravan, Colo., the Vanadium Corp. of America mills at Durango and Naturita, Colo., the Climax Uranium Co. mill at Grand Junction, Colo., and the Kerr-McGee Oil Industries, Inc. mill at Shiprock, N. Mex., retrieved V_2O_5 from ores. S. W. Shattuck Chemical Co., Denver, Colo., once recovered vanadium pentoxide, but this part of its operations was curtailed.

In 1958–59, only the Union Carbide Nuclear Co. mill (fig. 18) at Uravan, Colo., the Vanadium Corp. of America mill (fig. 19) at Durango, Colo., and the Climax Uranium Co. mill at Grand Junction, Colo., retrieved V_2O_5 from ores.

As the Nation's stockpile goal for vanadium was reached and as the AEC also had stockpiled vanadium, the AEC reduced its buying commitments to be consistent with obligations. Several AEC contracts were modified or extended in July 1958.

Union Carbide Nuclear Co.—The AEC obligation to purchase vanadium pentoxide from the company's mill at Rifle, Colo., was terminated. Liability for the purchase of vanadium pentoxide from the company's mill at Uravan, Colo., was reduced, and under certain operating conditions there was no liability for the purchase of vanadium.

Vanadium Corp. of America.—A contract, effective July 1, 1958, included no provisions for purchasing vanadium pentoxide produced at the Durango, Colo., mill.

Climax Uranium Co.—The previous contract with the AEC was to terminate October

FIGURE 18.—View of Uravan, Colo., Uranium-Vanadium Mill of Union Carbide Nuclear Co.

1, 1960, for their mill at Grand Junction, Colo.; after this date consideration was to be given to eliminating the vanadium commitment.

Kerr-McGee Oil Industries, Inc.—This company processes uranium-vanadium ores mined on the Navajo Indian Reservation. The company is required to pay for the vanadium content of ores meeting certain specifications. The AEC contract for purchasing uranium concentrate from this mill includes reinbursement for the vanadium content of certain ores. Instead of producing vanadium pentoxide, the mill tailings containing vanadium become the property of AEC.

Uranium Reduction Co.—This company operates a mill at Moab, Utah. Its contract with the AEC included payment for vanadium in tailings; the obligation for payment of vanadium in tailings terminated in 1959.

Atomic Energy Commission.—The AEC mill at Monticello, Utah, does not produce vanadium pentoxide, but pays for the vanadium content of ores meeting the specifications given in AEC Circular 5. Later, such ores may be sold to mills recovering vanadium pentoxide or may be treated at Monticello and the vanadium-bearing tailings stored for future processing. AEC commitments for purchasing vanadium terminate March 31, 1962.

As all but one of the Government ore-buying stations were closed in 1958, companies producing vanadium pentoxide either mined or purchased ores to make the V_2O_5 to be sold commercially.

MILLING PLANTS IN THE UNITED STATES

As the primary source of vanadium in the United States is the Four Corners area, many of the mills that process uranium-vanadium ores to make vanadium oxide (V_2O_5) are also in or adjacent to the Colorado Plateau, usually within a hundred miles of the supply-

FIGURE 19.—General View of Vanadium Corp. of America's Vanadium-Uranium Mill and Concentrating Plant at Durango, Colo.

ing mines. Mills on the plateau that have produced vanadium oxide are: Climax Uranium Co. (330 tons of ore per day), Grand Junction; Union Carbide Nuclear Co., Rifle and Uravan (fig. 18), 1,000 tons each of ore per day; Vanadium Corp of America, Durango (fig. 19), 750 tons of ore per day; and Naturita (closed down), all in Colorado; and Kerr-McGee Oil Industries, Shiprock, N. Mex. (300 tons of ore per day). Ore feed for these mills is either produced from their own mines or purchased.

In addition to mills on the plateau, other mills outside the plateau have contributed a small part of the vanadium oxide production. These mills are: S. W. Shattuck Chemical Co., Denver, Colo.; The Anaconda Co., Anaconda, Mont.; Columbia-Southern Chemical Corp., Jersey City, N. J.; F. W. Berk & Co., Wood-Ridge, N. J.; and Imperial Paper & Color Co., Glens Falls, N. Y.

The Anaconda Co. produced vanadium oxide at Anaconda, Mont., as a byproduct of phosphate products from vanadium-bearing phosphate rocks mined in Idaho. Vanadium oxide production at the Anaconda plant was suspended in 1954.

Vanadium-bearing chromite ores are used by Imperial Paper & Color Corp. and by Columbia-Southern Chemical Corp. as sources of vanadium compounds.

Although outside the Colorado Plateau, S. W. Shattuck Chemical Co., Denver, Colo., once utilized plateau ores to produce vanadium oxide. Another company, F. W. Berk & Co., Wood-Ridge, N.J., has used petroleum waste materials and chrome ores to make vanadium oxide and ammonium metavanadate.

The first step in producing vanadium in any of its forms is to recover the metal oxide from vanadium-bearing ores and convert the recovered product to vanadium pentoxide, V_2O_5, as given in the section on Metallurgy, page 47. The oxides produced at these mills and chemical companies are sold to other companies or shipped to producers' plants for conversion to ferrovanadium, vanadium metal, or various alloys or for subsequent use in the chemical, ceramic, or other industries.

FERROALLOYING PLANTS

A large part of the vanadium pentoxide produced at Grand Junction, Uravan, and Durango, Colo., was shipped to and converted into ferrovanadium at the plant of Union Carbide Metals Co. Alloy, W. Va. (fig. 20), and the plant of Vanadium Corp. of America, Cambridge, Ohio.

These two companies furnished vanadium products to industry, as shown in tables 1 through 10 in the section on "Uses," pages 5 to 16. They also export vanadium products and operate mines and plants in foreign countries. Details of the organization of the various producers of vanadium products follow.

MAJOR PRODUCERS

Union Carbide Metals Co.—Part of the company's activities center around the manufacture of ferroalloys, alloy metals, metal compounds, metals, and alloys for resisting abrasion, corrosion, and high temperatures. Some of the metal products include: Electrolytic chromium and molybdenum, tungsten, uranium, vanadium, and titanium metal.

The company operates numerous plants and properties throughout the United States and foreign countries.

The only plant of Union Carbide Metals Co. (fig. 20) which specifically manufactures vanadium products is at Alloy, W. Va. Union Carbide & Carbon Corp. (Union Carbide Nuclear Co.) operates vanadium-uranium mills at Rifle and Uravan, Colo.

Vanadium Corp. of America.—This corporation produces ores and manufactures and sells alloys, including ferrovanadium, ferrosilicon, ferrochromium, ferrotitanium, and other special alloys. It also produces special complex alloys of vanadium, titanium, chromium, and silicon in combination with one another and with aluminum, calcium, zirconium, manganese, and other elements.

Vanadium Corp. of America operates plants throughout the United States and holds mining property in several foreign countries, including vanadium mining claims of about 2,400 acres at Mina Ragra, Peru. At Mina Ragra, leaching, crushing, and drying plants are located near the property; however, operations in Peru were terminated in 1955. The corporation also owns or leases numerous mining claims and other vanadium-uranium ore properties in Colorado, Utah, Arizona, and New Mexico. The main operating properties are the leased Monument No. 2 mine in Arizona (fig. 21) and partly leased and partly owned deposits of autunite ore with pitchblend at Marysvale, Utah.

A one-third interest in 27 mining claims in the Long Park area of Colorado was acquired by Vanadium Corp. of America (*127*). These claims, known as the Eagle Basin group, extended over an area of 550 acres and gave the corporation additional uranium-vanadium reserves. Arrangements were also completed to lease 42 mining claims on a royalty basis from Marysvale Uranium Co. of Utah. The 42 claims cover about 850 acres in the Marysvale area near other properties operated by Vanadium Corp. of America. Ore is milled at the company's plant at Durango, Colo.

At Cambridge, Ohio, the Vanadium Corp. of America operates a ferroalloy plant that was completed early in 1954. Ferroalloys and commercial vanadium metal are produced at this plant. The plant has one electric arc furnace with an annual capacity of 6,000 net tons and houses two low-frequency induction-type furnaces with an annual capacity of 8,000 net tons of aluminum products and alloys. Products manufactured include ferrovanadium, ferrotitanium, grainal alloys, deoxidizing aluminum, and master alloys of aluminum. The company also has research laboratories at Cambridge, Ohio.

Climax Uranium Co.—A subsidiary of Climax Molybdenum Co., Climax Uranium Co., is engaged in mining and processing uranium-vanadium ores of the Colorado Plateau. At Grand Junction, Colo., this company operates a mill to treat ores obtained from mining properties formerly owned by Minerals Engineering Co., of Grand Junction, and from adjoining properties leased from the AEC. Vanadium pentoxide and uranium oxide are produced at the plant.

Kerr-McGee Oil Industries, Inc.—This company is concerned primarily with the production of petroleum products. In May 1952, Kerr-McGee Oil Industries, Inc., acquired the property of Navajo Uranium Co. The Navajo Uranium Division of Kerr-McGee Oil Industries, Inc., has uranium leases and permits in Wyoming and on the Navajo Indian Reservation in Arizona. The division operates a sampling plant and ore concentration plant, also a uranium concentrating mill at Shiprock, N. Mex., erected under AEC contract. Operations of the mill was begun in 1954. No vanadium pentoxide was produced at Shiprock in 1954, 1956, 1958, or 1959, but in 1955 and in 1957 vanadium brown cake and pentoxide were produced.

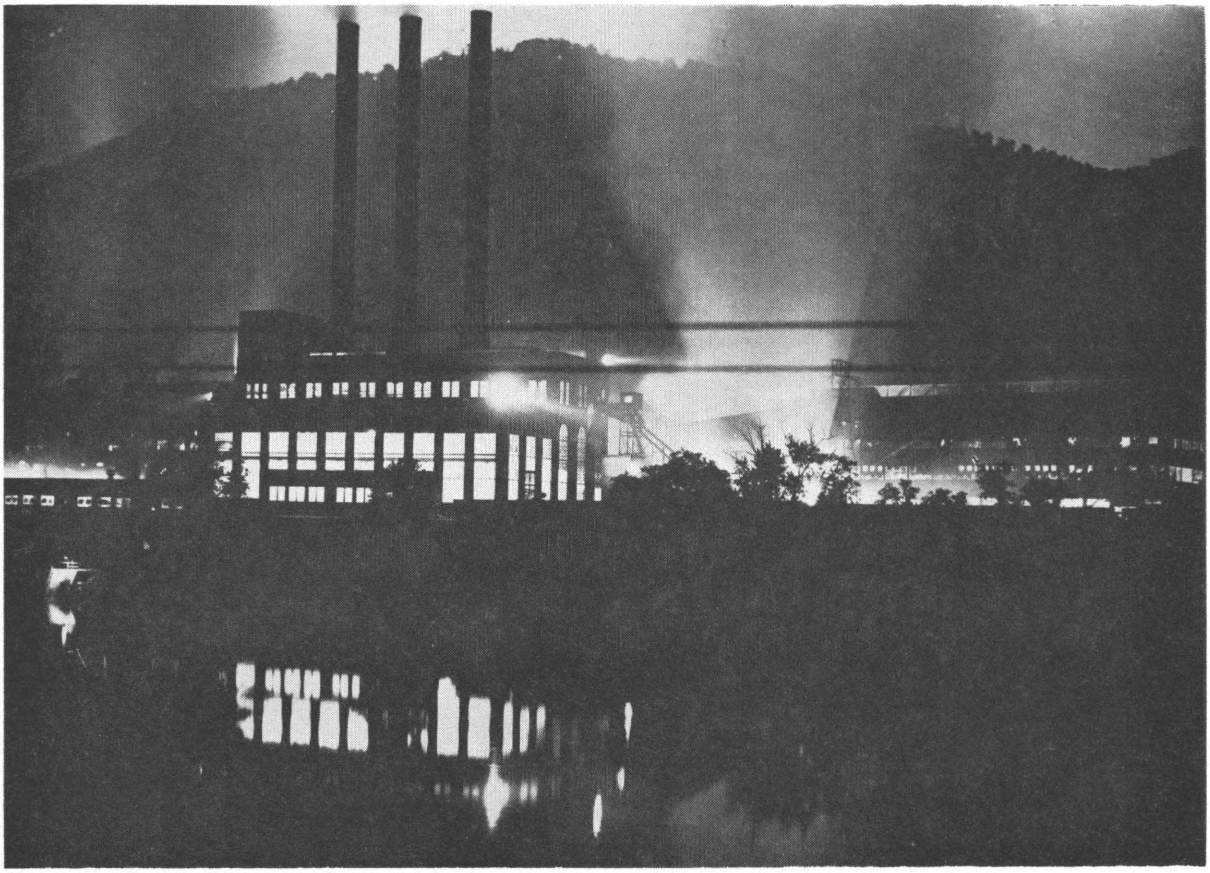

FIGURE 20.—Overall Night View of the Union Carbide Metals Co. Alloy Plant, Alloy, W. Va.

The Anaconda Co.—The Anaconda Co. formerly produced vanadium pentoxide as a byproduct in making treble superphosphate. Vanadium-bearing phosphate rock was mined at Conda, Idaho, and shipped to Anaconda, Mont., for processing. Production of vanadium pentoxide in conjunction with phosphate recovery was suspended in 1954.

Vitro Corp. of America.—This corporation produces coloring pigments for the paint and ceramic industries, porcelain enamels suitable for aluminum sheets, and descaling salts for use in the steel industry. It also conducts operations on the mining, refining, and processing of uranium ores and development and engineering research primarily in the field of atomic energy. In March 1956, the company purchased Uranium Prospectors Co., Ltd., Grand Junction, Colo. Vitro Manufacturing Co., a subsidiary of Vitro Corp. of America, operated a plant at Canonsburg, Pa., which produced vanadium oxide; however, no oxide was produced from 1954 through 1958.

Imperial Paper & Color Corp.—One of the plants of Imperial Paper & Color Corp., at Glens Falls, N.Y., produces small quantities of vanadium pentoxide from imported chrome ore. Products include wallpaper, chemical pigments, pigment colors, and chemicals.

Columbia-Southern Chemical Corp.—Columbia-Southern Chemical Corp. is a subsidiary of Pittsburgh Plate Glass Co. Small quantities of vanadium pentoxide are produced from imported chrome ores and used in manufacturing some of the company's products. This corporation produces soda ash used in making glass, soap, oil, textiles, drugs, pulp, and paper, also in water-softening purification processes and cleaning operations, and caustic soda used in manufacturing soap, chemicals, rayon, lye, and textiles, also in petroleum refining and rubber reclaiming. Other products include organic chemicals, ammonia, titanium compound, calcine, salt, liquid chloride and caustic, modified soda, special alkali, calcium choride, calcium hypochlorite, and other chemicals. Minor products include the manufacture of portland cement, insecticide, seed-grain disinfectants, dry colors, and fungicides.

FIGURE 21.—General View of Workings of Vanadium Corp. of America's Monument No. 2 Mine, Monument Valley, Utah.

CONSUMERS

Consumers of vanadium may be divided into two groups: Producer-consumers and buyer-consumers.

The first category, producer-consumers, includes companies that mine ore, extract vanadium oxide, and ultimately consume a large part of their oxide in making ferrovanadium and other alloys. These companies sell their products to buyer-consumers, such as steel companies, foundries, and other manufacturers, that consume ferrovanadium and alloys to make structural steel, iron and steel castings, tool steels, and other vanadium-bearing products for innumerable applications. It was estimated that about 275 companies in the latter category account for approximately 90 percent of domestic consumption. Ferrovanadium is the major item used by these consumers to produce vanadium-bearing products for industry and defense.

Vanadium pentoxide and ammonium metavanadate, raw-material products of producer-consumers, are used extensively but in small quantities by the chemical and related industries as catalysts. Examples of such users are petroleum refineries; sulfuric acid plants; and chemical plants producing ammonia, formaldehyde, malic anhydride, fumaric acid, and other products. Compounds of vanadium are utilized in manufacturing glass, ceramics, paints, varnish, and other materials. Although the market for vanadium compounds for chemical use is relatively small compared with that for alloying applications, applied research will undoubtedly create an ever-increasing market demand for vanadium compounds in chemicals.

Few new applications for vanadium metal, alloys, or compounds have been developed to alter basic consumer patterns. Because of its mechanical properties and chemical stability, vanadium may have many new applications as a cladding material, in reactors, in heat-resistant alloys, or in new chemical processes.

OTHER FREE WORLD NATIONS

Information on many facets of the vanadium industry in free world and Soviet bloc countries is fragmentary. World production of vanadium ore, exclusive of the United States, is generally considered to be confined to the Transvaal and South-West Africa, in the Union of South Africa, and Finland. Many Western European nations, including Germany, France, and Benelux countries, have recovered vanadium from slags. Some vanadium may also be retrieved from bauxite residue, especially in Germany, France, and Italy. Data on the names, locations, and capacities of ferroalloying plants was confined to brief sketches found in trade indexes and magazines.

ARGENTINA

Vanadium occurs in small, widely scattered deposits in the Provinces of Cordoba, Mendoza, and San Luis.

ENGLAND

The plants of Imperial Smelting Corp., Ltd., London, England, primarily make zinc and zinc products; however, various pigments and chemicals are also manufactured. Among the chemicals produced by this corporation is a vanadium catalyst (*104*, pp. 338–340).

Minworth Metals, Ltd., Forge Lane, Minworth, Birmingham, England (*104*, pp. 350–352) produces ferroalloys. The plant of this company has crushing, grinding, and classifying machinery; ore roasting and refining equipment; and smelting furnaces for reduction of ores. The aluminothermic reduction process is used to produce ferrotungsten, ferromolybdenum, ferrovanadium (50- to 60-percent or 75- to 80-percent), ferrotitanium, manganese metal, and chromium metal. Annual plant capacity was reported to be 2,500 tons of ferroalloys.

Magnesium Electron, Ltd., London, is one of the foremost producers of magnesium and magnesium alloys in Great Britain (*104*, p. 346). Other metals and alloys, including vanadium, are produced by this company. The main plant of the company is at Clifton Junction, near Manchester.

Another English company, Murex, Ltd., Rainham, Essex, England (*104*, p. 354) produces ferroalloys, nonferrous alloys, pure metals and powders, and metallic carbides. Plant facilities are on the banks of the Thames River at Rainham, Essex, England. Principal products of the company include ferrovanadium, ferrotungsten, ferrocolumbium, ferromolybdenum, ferrotitanium, ferromanganese, manganese metal, and chromium metal. Pure metals of most of these ferroalloys are manufactured, as well as metallic carbides and various combinations of nonferrous alloys.

FINLAND

The State-owned Otanmäki titaniferous iron deposit in central Finland contains a little vanadium, which is extracted with the iron and titanium.

Associated with the Otanmäki titaniferous iron deposits is a plant operated by Otanmäki Co., which produces vanadium pentoxide.

WEST GERMANY

The plant of Gesellshaft für Electrometallurgie at Fürth, near Nürnberg, produces ferrovanadium and other vanadium products from vanadium-bearing concentrates obtained from South-West Africa and other sources.

Ferroalloys and metals, including vanadium, may still be recovered and produced by Farbenfabriken Bayer, A. G., at Leverkusen, and at the Lunen plant of Vereinigte Aluminum-Werke, Bonn.

Another producer of vanadium and other rare metals in West Germany is the Otavi Minen und Eisenbahn-Gesellschaft. The plant of the company is at Frankfurt am Main, Neu-Isenburg (*104*, p. 248).

INDIA

The Dublabera Mining Co., Ltd., Dublabera, Bihar, India, has produced and exported small quantities of vanadium ore. Vanadium-bearing ore ranged from 0.28 and 1.92 percent and averaged about 0.96 percent vanadium.

The method for treating the local ore was developed by Christiania Stigerverk, Oslo, Norway, for Dublabera Mining Co., Ltd., Dublabera, Bihar, India.

ITALY

In Italy, the S.A.L.E.M. (Soc. p Az. Leghe e Metalli) with main offices in Genoa, produces vanadium in plants at Rapallo and Spigno Monferrato. Ferroalloys are produced at the Rapallo plant by the aluminothermic system (*104*, p. 267). Besides ferrovanadium, ferrotungsten, ferrotitanium, ferromolybdenum, manganese metal, chromium metal, and sodium and calcium tungstate are produced. Ferromolybdenum, ferrocarbon - vanadium, and ammonium-molybdenite are produced in the electric furnaces at the Spigno Monferrato plant. Capacity of the Rapallo plant was reported to be 5 tons a day and that of the Spigno Monferrato plant, 11 tons a day.

NETHERLANDS

One of the minor products of the Arnhem Tin Smelter (N.V. Hollandsche Metallurgische Bedrijven), with main offices at the Hague, is vanadium acid. Although this company primarily refines tin at its plant on the Rhine River, at Arnhem, it also produces solder, bearing metals, type metals, lead, antimonial lead and byproducts such as tungstic acid, tungsten salts, bismuth oxychloride, and vanadium acid (*104*, p. 270).

PERU

Mining operations at the Mina Ragra mine and associated mining properties of Vanadium Corp. of America in Peru were suspended owing to poor grade of ore and economic competition of uranium-vanadium production in the United States; however, the mine properties remain a potential source of vanadium ore and concentrate.

Milling facilities of Vanadium Corp. of America, at Mina Ragra and Jumasha, Peru, were shut down but remain in a standby condition.

NORTHERN RHODESIA

At Broken Hill, Northern Rhodesia, the Broken Hill Development Co. retrieved vanadium oxide from zinc-vanadium deposits from 1930 to 1952. Output was suspended in 1953, and all vanadium ore was reportedly stockpiled with mixed fines tailing pending evolution of a process for recovering both zinc and vanadium.

Facilities for producing vanadium oxide are not known to exist at Broken Hill Development Co., Northern Rhodesia, since production was suspended.

SOUTH-WEST AFRICA

In South-West Africa, the South-West Africa Co., Ltd., produces vanadium-bearing ore from their Abenab West and Berg Aukas mines (*125*). Other mining properties investigated for possible production of vanadium ore include Harasib and Baltika, as the vanadium content of ores in the Abenab West and Berg Aukas mines was low.

The South-West Africa Co., Ltd., produces a vanadium concentrate. In the past, some of the concentrate was shipped to Belgium where it was processed to fused vanadium oxide for the company.

TRANSVAAL

In the Transvaal, Union of South Africa, vanadium ore deposits, reportedly containing more than 50 million pounds of recoverable vanadium pentoxide, were developed by Minerals Engineering Co., Ltd. (*136*).

Two U.S. companies, Minerals Engineering Co. and Rockefeller Center, Inc., and an English concern, High Speed Steel Alloys, Ltd., of Lanchashire, England, constructed a vanadium mill in the Transvaal, Union of South Africa (*138*). The mill, located near Pretoria, was reported to have an annual capacity of 3,600,000 pounds of vanadium concentrate and was scheduled for completion in September 1957.

SOVIET BLOC

Near the Magnitka deposits (east of Kusa) in the Chelyabinsk Oblast' of the Urals, U.S.S.R., ores of several ferroalloys occur. From these ores, special steels are produced at the Chelyabinsk ferroalloy works (*104*, pp. 417–418).

Vanadium salts, electrolytic and refined copper, soft lead, red lead, zinc oxide for paints, zinc sulfate, pure selenium, cement, cadmium, silver, gold, platinum, sulfuric acid, and palladium were reported produced at the Kombinat "Wilhelm Pieck," Eisleben, East Germany (*104*, pp. 230–231). This company was formerly called the Mansfelder Kupferschiefbergbau, A. G., and later Mansfelder Kupferbergbau und Huttenwerk, which was a publicly owned concern belonging to VVB Mansfeld, Eisleben.

CHAPTER 8. RESEARCH AND DEVELOPMENT

The major part of the research on vanadium and its alloys since 1955 has been intensive and rather broad in scope. Experimentation to find new methods of extracting vanadium from ores, producing a high-purity metal, and developing useful vanadium alloys has been conducted in the United States by research institutes, universities, industry, and the Government, including the Navy, Air Force, Atomic Energy Commission, and Bureau of Mines. The total expenditure for vanadium research is not known, as it is connected with other activities. However, from 1955 to 1959 it was probably less than $500,000 annually.

Industry has been concerned with improving products and finding new markets. Its research at mines and mills has improved extractive methods and techniques and has resulted in the production of purer vanadium oxide needed in making high-purity metal and alloys. Research by industry in 1959 included purification of vanadium compounds for subsequent reduction to metal, improvement of remelting techniques, and development of hot and cold methods of working vanadium metal. Experimentation with new or improved ways of making high-purity vanadium metal was a significant part of industry's research. In addition, considerable time was devoted to devise and improve methods of making rod, tube, sheet, and wire of high-purity vanadium. Small shipments of vanadium metal to alloy manufacturers indicated that attention was being directed to the development of alloys using high-purity metals. Additional research by industry was conducted on developing vanadium-bearing alloys. Details of industrial research may be found in the chapter, "Properties, Products, and Uses," page 5.

Perhaps the greatest research effort on vanadium (1955–59) was under Government sponsorship. The scope of the Government research program was broad. Fields of interest ranged from extractive metallurgy to the development of new methods of producing a high-purity, ductile vanadium metal.

One part of the research activities of the Bureau of Mines dealt with the recovery and purification of vanadium compounds from ores and industrial wastes. This pioneering research by Bureau personnel led to the development and subsequent adoption by industry of a solvent extraction process to recover vanadium from ores. Another facet of the Bureau's research included the preparation and purification of compounds suitable for reduction to metal. Bomb and open-crucible reduction methods were used to make a commercial-grade vanadium metal and a vanadium-titanium-aluminum alloy. High-purity vanadium was also produced by bomb-reduction techniques. A different approach for making high-purity vanadium by fused-salt electrolysis was pioneered by Bureau researchers. This method of making vanadium metal produced a soft, ductile product. The scope of the Bureau's research included the analysis and determination of the properties of high-purity vanadium metal and alloys and evaluation of the effects of vanadium melted by electron beam bombardment. Resistance of vanadium metal and vanadium-bearing alloys to chemical and galvanic corrosion, when immersed in sea water and in certain organic and inorganic liquids, was also part of the Bureau's research program on vanadium.

Other Government agencies that conducted research on vanadium placed greater weight on different areas of endeavor. Emphasis on vanadium research for the Navy and the Air Force, conducted by a research foundation, was on vanadium alloys, especially binary and ternary alloys. The AEC has supported several research projects in which vanadium was included for study.

To fit the exacting requirements of high-temperature or other special applications, research has been intensified on many of the refractory metals. Vanadium, as one of these metals, has many good characteristics, but it also has limitations. Much must be ascertained on the properties of vanadium and on its alloying and fabrication characteristics. The oxidation behavior of vanadium, the attributes or deficiencies of other alloying elements when added singly or in combination, and the determination and compilation of basic and analytical data are needed to expand the uses of vanadium.

Because vanadium oxidizes at moderately high temperatures, new applications for the metal or its alloys at elevated temperatures are limited at this time. Continued research may eventually reveal numerous uses for vanadium metal and its alloys.

Apart from the application of vanadium as a metal or an alloying element, new and greater uses may be found for certain vanadium compounds in the chemical and related industries. Research on developing methods of reducing the objectional smog-contributing components of automobile exhaust fumes may foster the use of vanadium. Several ways have been devised to reduce the hydrocarbon content of exhaust gases 60 to 90 percent. One method under development uses a vanadium pentoxide and aluminum catalysts.

CHAPTER 9. LEGISLATION AND GOVERNMENT CONTROLS

OFFICE OF MINERALS EXPLORATION

Federal financial assistance for the discovery of mineral reserves, excluding organic fuels, the United States, its Territories, and possession, was authorized, under Public Law 701, 85th Congress, 2d session. The Office of Minerals Exploration (OME), formerly the Defense Minerals Exploration Administration, was established under the U.S. Department of the Interior to carry out this law. Under published regulations (title 30, "Code of Federal Regulations", ch. 111), the OME will participate in a part of the cost of exploration for certain minerals or mineral products. Vanadium was not included among the minerals eligible under this program; however, exploration for uranium ores, many of which contain vanadium, may receive assistance. A clause in the standard contracts between the operator or producer of uranium ore and the OME stipulates that a royalty shall be paid the Government on all minerals and metals mined or produced which could include vanadium.

Details on payment of the V_2O_5 content of certain ores by the Atomic Energy Commission is given in the section entitled "Ore Buying Stations and Mills" in the chapter, "Structure of the Vanadium Industry," page 71. Payment of the V_2O_5 content of uranium-vanadium ores has stimulated uranium production and thus increased vanadium production. Payment of the V_2O_5 content of uranium-vanadium ores was on a contract basis.

WORLD WAR II CONTROLS

Information on the history of Government controls during World War II may be found in numerous publications, including "War Production Controls" (*70*), "Strategic Minerals" (*61*), and "Federal Records of World War II, 1950" (*75*). Specific references to control orders pertaining to vanadium may be found in various supplements to the "Code of Federal Regulations of the United States of America," dating from 1938, under title 32 and primarily in chapter IX. These references include General Metals Order No. 1, "M" (conservation) Orders, and "L" (limitation) Orders. Maximum Price Regulations are found under title 32 but in chapter XI. The "Code of Federal Regulations of the United States of America" gives references to specific orders and amendments to order that appear in the "Federal Register" by volume and page number.

Executive Order 9638, which abolished the War Production Board and placed the control of certain strategic materials under the Civilian Production Administration, appeared in the 1945 supplement of the "Code of Federal Regulations of the United States," under title 3, chapter II.

Various forms used to obtain factual and statistical information during World War II may be found in "Catalogue of War Production Board Reporting and Application Forms," published by the Bureau of Demobilization, Civilian Production, Office of Temporary Controls. Volume X of the series of publications is the commodity index. Volume I contains forms dealing with vanadium, steel, other ferrous additives, copper, aluminum, and manganese.

Control orders were issued by the Office of Production Management, the War Production Board, the Office of Price Administration, the Civilian Production Administration, and the Office of Temporary Controls. Summaries of regulations may be found in Bureau of Mines "Minerals Yearbooks," 1941 to 1945.

Vanadium was listed among the metals included in the inventory control provided by General Metals Order 1, May 1, 1941, issued by the Office of Production Management (*150*) (succeeded by the War Production Board). Vanadium was removed from this order August 14, 1941, and placed under full priority control effective September 1, 1941. This new regulation (Order M–23) gave high priorities to all defense orders for vanadium and required that they be given preference over nondefense orders. Purchasers of vanadium were required to file a statement of intended uses not later than the 25th of the month preceding the date specified for delivery. Further provisions of the order stated that deliveries would be restricted to an amount not in excess of that needed to fill a given manufacturer's orders, based upon his current method and rate of production. General Preference Order M–23–a, issued

December 20, 1941, replaced the previous priority-control order. This order provided for monthly requests for vanadium allotments. It authorized the Director of Priorities to make monthly allocations without regard to previous preference ratings. According to this order, consumers receiving less than 50 pounds a month were not obliged to file reports. As originally announced, the order was to be effective until June 30, 1942.

Vanadium was 1 of the 13 materials listed in General Import Order M–63, which went into effect December 28, 1941. The Government also had complete control of imports under General Import Order M–63. This order stipulated that, unless authorized by the Office of Production Management (OPM), all future contracts for these materials would be handled by the Metals Reserve Company, (MRC), the Reconstruction Finance Corporation (RFC), or other Government agencies. Accordingly, no private person or concern could make arrangements for processing and immediate reexport; the Director of Priorities could grant specific exceptions to the order.

The melting of vanadium was made subject to approval of the melter's schedule in an amendment to Order M–23–a dated June 23, 1942 (*150*). According to this amendment, the limit of unrestricted deliveries of vanadium was lowered from 50 to 10 pounds per month.

An amendment to Order M–23–a issued December 26, 1942, defined vanadium as including ores and concentrates, primary waste compounds, vanadium alloys, and waste products such as flue dust. The amendment also stipulated that ferrovanadium producers were exempt from melting restrictions and could freely acquire vanadium raw materials and that no authorization was required for melting 10 pounds of vanadium per month.

Allocation control of vanadium by the War Production Board, which had been in effect since December 20, 1941, was removed December 30, 1943, by amendment to General Preference Order M–23–a (*150*). Vendors of more than 500 pounds of vanadium (ferrovandium and commercial vanadium pentoxide) in any one month were required (henceforth) to report all sales to the War Production Board.

Order M–21–h,[12] dealing with restrictions imposed by the War Production Board on the use of vanadium in melting alloy steels, as revoked in January 1944. Revoking this order allowed producers of alloy steels to use any alloy content but stipulated the use of 50 to 60 percent of alloy scrap in all melts.

General Limitations Order L–223,[13] revoked early in January 1944, removed War Production Board restrictions on the distribution, sale, and use of hard-facing alloys containing vanadium and certain other metals.

Order M–21–a provided for submission of melt schedules to the Board for authorization of the use of vanadium in alloy steels (*150*).

Effective October 1, 1944, imports of vanadium ceased to be subject to Government control under General Imports Order M–63.

Several noteworthy changes took place in 1945 in the various wartime regulations and controls. The War Production Board General Preference Order M–23–a (vanadium) was revoked June 5, 1945. Authority to regulate the production, distribution, and use of this metal then resided in General Preference Order M–21 of May 4, 1945 (as amended)—iron and steel production (*150*). Order M–21 specified that alloy steel and alloy iron should not be melted except upon approval by the War Production Board and that producers of alloying materials, whether ferroalloys or other compounds usable in iron and steel, should file monthly production records with the Board. Order M–21 (as amended) was reissued August 24, 1945, and provided that the Board might issue from time to time directions that would regulate the production and distribution of alloy steel and iron and ferroalloys and alloying compounds.

Close formal control over vanadium or its products was not exercised in 1945; however, controls could have been reestablished under General Preference Order M–21.

The War Production Board was abolished and the Civilian Production Administration was established by Executive Order 9638, November 3, 1945. The Civilian Production Administration then assumed the controls formerly exercised by the Board on the production and use of vanadium products. Other Government organizations exercised control over domestic production and prices.

Early in World War II, both industry and the Government were active in expanding plant capacity. In 1941–42, Vanadium Corp. of America, through a lease agreement with the Defense Plant Corporation, built an ore treating plant of 120 tons capacity at Monticello, Utah, which was to be operated for the

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[12] Order M–21–h was concerned with the conservation of the supply and control over the distribution of tool steel, alloy steel (Order M–21–a), class A high-speed steels, and class B steels.

[13] General Limitations Order L–223 was concerned with restrictions on the delivery of hard-facing materials.

Metals Reserve Company. The plant cost $875,000 (*150*). Funds were provided by the Defense Plant Corporation.

In preparing for expanded production of vanadium, the principal producers, in cooperation with Government agencies, built roads, opened ore purchasing depots, and established other facilities in newly opened areas of the Colorado Plateau to increase ore production and subsequent vanadium production. Besides the Metals Reserve Company plant operated by Vanadium Corp. of America, another mill at Durango, Colo., was operated for the Metals Reserve Company by United States Vanadium Corp. In addition to Government-owned mills, several privately owned mills were operated in the Colorado Plateau area.

In 1942, consideration was directed toward developing the Lake Sanford titaniferous magnetite deposits in New York State. Although no wartime agencies were involved in these investigations, it is noteworthy that the Bureau of Mines, the National Lead Co., and the University of Minnesota worked on extracting vanadium but made no commercial recovery (*150*).

Record-breaking mine output of vanadium ores and concentrates in 1943 was attributed to the policies of the Metals Reserve Company. United States Vanadium Corp. and Vanadium Corp. of America contributed immeasurably to the success of Metals Reserve Company program.

DOMESTIC PRICE CONTROLS

Another item fostering greater mine production was the price incentive program begun by the Metals Reserve Company. In 1942, before the Metals Reserve Company entered the ore purchasing field, ore production was concentrated in the hands of a few operators. With the advent of the ore purchasing and price incentive program of the Metals Reserve Company, ore production was increased. Small or independent operators were much more numerous and contributed about half of the Government-account purchases in 1943 (*150*).

By early 1943, production had exceeded consumption. As a large part of domestic vanadium production was marginal in nature and as supplies were not critical, the Metals Reserve Company terminated the Government-supported purchase program on February 29, 1944. The processing plants at Durango, Colo., and Monticello, Utah, were shut down but were left in standby condition.

Termination of the supported ore purchasing program caused a rapid and marked decline in the number of small independent mine operators, and the maintenance of a domestic vanadium industry reverted to the two major producers, Vanadium Corp. of America and United States Vanadium Corp. —now Union Carbide Nuclear Co. (*150*). These two companies severed connections as agents for the Metals Reserve Company, and their mining and milling operations by the end of 1944 were largely for private account. Most of the Government-owned stocks of ores and concentrates were sold to United States Vanadium Corp. in 1944, and the Defense Plant Corporation leased the Monticello, Utah, mill to Vanadium Corp. of America early in 1945.

Control over prices of vanadium ores, concentrates, and products was not exercised in 1941. An informal agreement was reached in the autumn of 1941 between producers and the Office of Price Administration not to increase the prices without notice to that agency (*150*). On April 28, 1942, this tentative arrangement was succeeded by the General Maximum Price Regulation, which froze prices at existing levels. These ceiling prices became fixed under terms of Maximum Price Regulation (MPR) 489, effective November 8, 1943. This regulation did not govern the price of vanadium ore. No standard price schedule was issued by the Metals Reserve Company on ores, and all purchases by the agency were made on the basis of individual contract. Among factors affecting ore prices were distance from purchase depot and grade of ore.

Although prices of ores were not regulated, maximum price regulation 489 did provide for the following prices for ferrovanadium and vanadium pentoxide. These prices remained in effect throughout 1944 (*150*).

Ferrovanadium.—Per pound of contained vanadium, standard crushed size, f.o.b. Niagara Falls, N.Y., or Bridgeville, Pa., freight allowed to destination for 25 pounds or over:

A, Open Hearth, minimum 30 percent V (trade journal, quotations specify a minimum of 35 percent vanadium)	$2.70
B, Crucible, minimum 35 percent V	2.80
C, Primos, minimum 35 percent V	2.90

(Spot prices, 10 cents per pound higher)

Vanadium pentoxide.—Per pound of contained V_2O_5 air-dried or fused vanadium pentoxide, f.o.b. Niagara Falls, N.Y., or Bridgeville, Pa., with freight allowed to destination on 25 pounds or over:

1, Maximum base contract price, any quantity	$1.10
2, Maximum base spot price:	
500 pounds and over	1.15
Less than 500 to 10 pounds	1.20
Under 10 pounds	1.25

A nominal price of 27½ cents per pound had been quoted for the V_2O_5 content of ores since early in 1935. This price did not prevail during the war because there was a market by grades among mill operators. The average value of shipments was 31 cents per pound in 1942, and prices as high as 50 cents were reported in sales to Metals Reserves Company Agencies (*150*). In 1943 the average price paid rose to about 35 cents per pound of contained vandium pentoxide (*150*). This increase in price was due largely to a full year's buying program, a substantial share of which was for Government account (Metals Reserve Company) at somewhat above the early free-market prices. Private buyers purchased upon a sliding-scale basis that depended primarily upon the V_2O_5 content with a minimum near 2 percent. Before the United States entered World War II, prices reported to the Bureau of Mines ranged from about 18 to 35 cents or more for various standard grades and classes. No consideration was given to the uranium content of the ore, which then had a limited market and frequently was too low to have commercial value. To stimulate production, especially by small operators, the Metals Reserve Company, in 1942–43 purchased ore that was unacceptable because of its low grade or refractory nature and set prices virtually on a single-lot basis, giving consideration to the higher labor and supply costs and the length of haul to purchase depot or processing plant. Although no fixed purchasing schedule was effective, delivered prices of ore appeared to have been about 50 to 75 percent above prewar levels.

General trade quotations for V_2O_5 content of ore, vanadium oxide, and ferrovanadium remained unchanged during the war period, 1941–46. Vanadium pentoxide in ore was quoted at 27½ cents per pound, technical-grade vanadium oxide was quoted at $1.10 per pound of contained V_2O_5, and ferrovanadium of various grades was quoted at $2.70 to $2.90 per pound of contained vanadium. In 1945 ferrovanadium was quoted at $2.75 to $2.90 per pound of contained vanadium. From January 1 to December 12, 1946, the 1945 quotation for ferrovanadium remained in effect; however, from December 12 to December 31, the price was reduced to $2.70 to $2.90 per pound of contained vanadium.

Under the terms of Maximum Price Regulation 489, effective November 8, 1943, the following prices on vanadium products were frozen at existing levels (*150*).

Contained vanadium in *ferrovanadium* for standard crushed sizes f.o.b. Niagara Falls, N.Y., or Bridgeville, Pa., freight allowed to destination for 25 pounds or over:

Premiums per pound of contained vanadium for crushing or grinding to sizes smaller than standard were added.

Grade	Analysis, percent			Prices	
	Vanadium (minimum)	Silicon (maximum)	Carbon (maximum)	Contract	Spot
A– Open Hearth	30	12.00	3.50	$2.70	$2.80
B– Crucible	35	4.00	1.00	2.80	2.90
C– Primos	35	1.50	.20	2.90	3.00

Maximum prices per pound of contained V_2O_5 in vanadium f.o.b. Niagara Falls, N.Y., or Bridgeville, Pa., with freight allowed to destination on 25 pounds or over, were established at:

1, Maximum base contract price, any quantity	$1.10
2, Maximum base spot price:	
500 pounds and over	1.15
Less than 500 to 10 pounds	1.20
Under 10 pounds	1.25

Premiums per pound of contained V_2O_5 for crushing or grinding to sizes smaller than the standard may be added.

Prices for vanadium products, as established under MPR 489, were finally suspended by Amendment 26 to Supplementary Order 129 on June 12, 1946 (*150*).

TARIFFS

Domestic tariff regulations on vanadium imports include raw materials and products. Some materials enter duty free (free list). On other materials or products, a duty is payable under some particular provision of the Tariff Act of 1930 (the Act) as amended.[14]

Vanadium materials that can enter the United States duty free are vanadium ores and concentrates and flue dust and boiler scale containing vanadium.

The tariff status of vanadium ore was described in U.S. Tariff Commission's "Summaries of Tariff Information" (vol. 16, pt. 3, par. 1719), which states "vanadium ore or concentrates are classified as minerals, crude, or not advanced in value or condition by refining or grinding, or by other process of manufacture n.s.p.f." (not specially provided for). Vanadium ore and concentrates are admitted duty free under the Tariff Act of 1930; this duty-free status of vanadium ore was bound in the Torquay Agreement, October 7, 1951.

Vanadium-bearing flue dust and boiler scale were covered in provisions of the Tariff Act of 1930, as amended. Paragraph 1664 includes: "Metallic mineral substanced in a crude state, such as brass foundry ash, drosses, flue dust, residues, and skimmings, n.s.p.f."[15]

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[14] Statutory rates of duty are currently applicable to products of Communist dominated or controlled countries or areas designated (during 1951–53) by the President pursuant to sec. 5 of the Trade Agreements Extension Act of 1951.

[15] U.S. Tariff Commission, United States Import Duties (1954); Misc. Ser. TC 1.10:Im 7/4/952, 1952, p. 237.

The classification of imports of vanadium products (metals and manufactures) was covered in the Act (1930) as amended.

Paragraph 302(n) regulates the importation of vanadium metal. Under the Act, a 25-percent tariff rate prevailed. In June 1951, this rate was reduced to 12½ percent.

The tariff rate for ferrovanadium was covered in paragraph 302(m) of the Act of 1930; the rate was 25 percent. This rate was reduced to 15 percent in a trade agreement effective January 1936 and January 1939. In 1948 (Geneva), the rate was again reduced to 12½ percent.

Under the provisions of paragraphs 301 and 305, certain iron and steel products were subject to additional duties on specified vanadium contents.

Provisions of paragraph 301 of the Act (1930) provided for a duty of $1 per pound of alloy content. Pursuant to concessions granted by the United States in the General Agreement on Tariffs and Trade (GATT) of July 11, 1948, the rate was reduced to 50 cents. The statutory rate of vanadium content in excess of 1/10 of 1 percent in granular or sponge iron was $1. per pound. Under GATT, April 30, 1950, the rate was set at 50 cents per pound.

Paragraph 305 relates to all steel and iron in the products described and enumerated in paragraphs 303, 304, 307, 308, 312, 313, 315–319, 322–324, 327, and 328 of the Act (1930), containing more than 1/10 of 1 percent vanadium and valued at over 3½ but not over 8 cents per pound. Under the Act (1930), the statutory rate was 8 percent plus $1. on vanadium content over 0.1 percent. Trade-agreement modifications of the 1930 Act reduced the rate to 4 percent plus $1. per pound on vanadium content over 1/10 of 1 percent on August 5, 1935 (Sweden). On January 1, 1948 (GATT—Geneva), the rate was further reduced to 4 percent plus 50 cents on vanadium content over 1/10 of 1 percent.

Paragraph 302(1) of the Act (1930) pertains to imports of vanadium carbide and chromium vanadium. According to the Act, (1930), there was a 25-percent ad valorem duty on these materials. In June 1951, this rate was reduced to 12½ percent.

Ferroaluminum vanadium, ferromanganese vanadium, ferrosilicon vanadium, and ferrosilicon aluminum vanadium were dutiable under paragraph 302(m) of the Act (1930) at 25 percent ad valorem. The Torquay Agreement of June 1951 reduced this rate to 12½ percent.

Alloys of two or more of the elements barium, boron, calcium, strontium, thorium, titanium, vanadium, and zirconium were dutiable under paragraph 302(n) of the Tariff Act of 1930 as amended. Under the Act, (1930), a tariff rate of 25 percent ad valorem applied. This rate was reduced to 12½ percent in June 1951. If alloys of these materials contain uranium the 25-percent-ad-valorem rate was applicable.

Alloys of two or more of the metals columbium, niobium, or tantalum and alloys of one or more of the metals barium, boron, calcium, strontium, thorium, titanium, vanadium, or zirconium were provided for in the Act (1930). Under the Tariff Act of 1930, the rate was 25 percent ad valorem. In 1948, under the Geneva Agreement, the rate was reduced to 12½ percent. If uranium was present, the 25-percent rate applied.

Alloys, n.s.p.f., of one or more of the metals barium, boron, calcium, columbium, niobium, strontium, tantalum, thorium, titanium, vanadium, or zirconium with one or more of the metals aluminum, chromium, cobalt, copper, manganese, nickel or silicon are also dutiable under paragraph 302(n). Under the Act (1930), a 25-percent duty was applicable. In August 1951, this rate (except if containing titanium and uranium) was reduced to 20 percent. On June 30, 1956, the rate was further reduced to 19 percent; on June 30, 1957, to 18 percent; and on June 30, 1958, to 17 percent. Exceptions to these rates were alloys containing titanium, which were dutiable at 20 percent and alloys with uranium which were dutiable at 25 percent.

Paragraph 344 of the Act (1930) was concerned with tariff rates on cylindrical steel rolls, ground and polished, containing more than 1/10 of 1 percent of vanadium. Under the Act, the rate was 40 percent ad valorem. By an agreement effective June 30, 1956, the rate was reduced to 38 percent. The rate was reduced to 36 percent on June 30, 1958.

Cutting tools of any kind containing 1/10 of 1 percent of vanadium were dutiable under paragraph 352 of the Tariff Act of 1930 at 60 percent. In 1948 (Geneva Agreement), the rate was reduced to 30 percent ad valorem.

Vanadic acid, vanadic anhydride, salts of the foregoing, and chemical compounds, mixtures, and salts, wholly or in chief value of vanadium and not specially provided for, were in paragraph 91 of the Act (1930). The tariff rate for these materials was established at 40 percent ad valorem.

Many products containing vanadium were dutiable under various other provisions of the Tariff Act of 1930.

CONTROLS BY FOREIGN COUNTRIES

Vanadium raw materials and products have been exported primarily to Western and Southern European nations. As these nations apparently are not self-sufficient in supplies of vanadium and as the United States is an exporter of vanadium raw materials and products, the import regulations of these nations could be significant factors in determining future supply and demand problems. Recent developments in vanadium production in Finland and South Africa may alter this situation. However, the nations that have been taking most U.S. exports are Canada, Austria, Belgium-Luxembroug, France, West Germany, Italy, Japan, Sweden, Switzerland, and Spain.

The data on import regulations, tariffs, and quotas for these nations was furnished by the Bureau of Foreign Commerce. Because of the complexity of import regulations, it was difficult to make direct comparisons between nations. Moreover, because of differences in reporting procedure and terminology, the following information does not cover all regulations that might have been imposed upon vanadium raw materials and products imported into the respective countries. The data may better be used as a guide in determining import regulations rather than as an exhaustive study of tariff rules and regulations.

AUSTRIA

This nation does not have any import quotas on vanadium or vanadium products. Ore containing vanadium, ferrovanadium, and vanadium chemicals requires an import license in addition to an exchange permit before it can enter the country. Vanadium metal may be imported to Austria without an import license and payment permits will be granted automatically. Table 25 gives import duties on vanadium and vanadium chemicals imported into Austria.

BRAZIL

Brazilian import and exchange control regulations group commodities into five categories according to their degree of essentiality to the national economy. The most important commodities were listed in the first category. All commodities not specifically given in the first four categories were included in the last or fifth (luxury) category. For each of the five categories, exchange commitment certificates were auctioned. These certificates entitled the holder to apply for an import license required for all importation. Importers could pay the official rate of exchange, which in 1956 was 18.82 cruzeiros to the dollar, in addition to the auction bid or premiums. Small amounts of exchange were auctioned in the fourth and fifth categories; consequently, the auction bids in these categories were very high, making the importation of commodities in these groups very expensive in terms of cruzeiros. Ferrovanadium and vanadium oxide were included in the second category of the Brazilian import and exchange control system. Vanadium metal and its alloys were included in the fourth category of this system, and the other vanadium materials appeared to be included in the fifth category. Table 26 shows the tariff number under which duties on vanadium ores, alloys, metals, and unclassified materials were given. Besides the duties indicated, there were items of importance such as consular fees, fines, and other duties applicable to the import tariff system. The Brazilian control system was given in World Trade Information Service Publication, Part II, No. 56–1, Licensing and Exchange Controls of Brazil.

TABLE 25.—*Rates of import duty on vanadium raw materials and products into Austria* [1]

Tariff No.	Form	Ad valorem, percent	Turnover-equalization tax, percent of duty-paid value
Ex. 109	Ores containing vanadium	Free	Free.
Ex. 412 (c)	Vanadium metal	do	Do.
Ex. 365(c4)	Ferrovanadium	do	Do.
Ex. 511	Vanadium chemicals (although vanadium chemicals are not specified in the Austrian tariff schedule, we believe they are covered in the general category of auxiliary chemicals, n.e.s.):		
	(a) In packages of 5 kilos or more	10	5.25
	(b) In packages of less than 5 kilos	15	5.25

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

Vanadium metal may be imported into Austria without import license; payments permit will be granted automatically.

Ores containing vanadium, ferrovanadium, and vanadium chemicals require an import license in addition to an exchange permit.

BELGIUM-NETHERLANDS-LUXEMBOURG

The Benelux countries have had a common tariff in effect since January 1, 1948, which subjects imports from non-Benelux countries to the same rate of duties. Like import regulations of other countries, various other controls were applied to the importation of vanadium and vanadium raw materials and products to the Benelux countries. These con-

TABLE 26.—*Rates of import duty on vanadium raw materials and products into Brazil*[1]

Tariff No.	Form	Dutiable unit	Minimum rate, percent
596	Unspecified metallic mineral ores	Ad valorem.	15
798	Iron and steel and their alloys: Cast, pig, or puddled, unwrought in blocks, ingots or lumps; scrap and old iron (This article includes all kinds of steel, special or not, and also ferrometallic alloys and ferroalloys, being considered as such those in which the percentage of metal most heavily taxed is less than 50 percent. From 50 to 70 percent, such alloys will be subject to half the rate applied to the most heavily taxed metal, and will pay the full rate thereof when the percentage exceeds 70 percent.)	Gross ton	[2] 458.64
985	Any unclassified metalloids, metals, and their alloys	Ad valorem.	25
984	Unclassified raw materials and preparations	do	25
1231	Any unclassified chemical product, organic or inorganic	do	25

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, October 3, 1956.

[2] In cruzeiros; 18.32 cruzeiros to the dollar, Sept. 21, 1956.

Also applicable are a surtax of 10 percent of the duty and a social security tax of 4 percent ad valorem.

trols included regulations, duties, taxes, and licenses. Import duties on some vanadium commodities are given in table 27. The Bureau of Foreign Commerce, U.S. Department of Commerce, can give complete details on particular commodities.

CANADA

Rates of import duties on vanadium ore, ferrovanadium, vanadium metal, and other vanadium products and derivatives are given in table 28 for Canada. Besides import duties, a general sales tax of 10 percent (1956) was imposed on domestic and imported materials; however, this tax was not collected on materials consumed or expended in the manufacture of goods.

FEDERAL REPUBLIC OF GERMANY

Import duties on vanadium ores, vanadium metal, chemicals, and derivatives are shown in table 29 for the Federal Republic of Germany.

FRANCE

Table 30 gives rates of import duty on vanadium and various vanadium derivatives and chemicals for France. Pertinent data on import regulations are given in the note at the bottom of this table. In addition to vanadium and vanadium compounds, various other metals and derivatives are shown.

TABLE 27.—*Rates of import duty on vanadium raw materials and products into the Benelux Nations* [1] [2]

Tariff No.	Form	Import duty	Netherlands import tax of duty and tax-paid value, percent	Belgium transmission tax of duty-paid value, percent
195	Ores, concentrated or net: (1) Other	Free	Free	5
232	Oxides and hydroxides, n.e.s.:			
	(c) Vanadium pentoxide	do	5	5
	(g) Others	do	5	5
697	Ferroalloys: (2) Others: (h) Ferrovanadium	do	5	5
800	Metals and alloys, not worked: (e) Cobalt, cadmium, tungsten, others	do	5	5

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

[2] Belgium-Netherlands-Luxembourg (Benelux).

NOTE.—The above products enter free of import restrictions; exchange is freely granted.

TABLE 28.—*Rates of import duty on vanadium raw materials and products into Canada* [1]

Tariff No.	Form	Imports from (ad valorem, percent) —	
		British Empire	United States
Ex. 329	Vanadium ore and vanadium concentrates	Free	Free.
Ex. 375(f)	Ferrovanadium used in the manufacture of iron or steel	do	5
Ex. 711	Vanadium metal	15	20
Ex. 208(g)	Vanadium oxide, whether in powder, in lumps, or formed into briquettes by use of a binding material, when for use in the manufacture of steel, under regulations prescribed by the Minister of National Revenue	Free	Free.
Ex. 490(a)	Vanadium preparations for use as catalysts	do	Do.
Ex. 711	Vanadium derivatives and chemicals of a class or kind made in Canada	15	20
Ex. 208(t)	Vanadium derivatives and chemicals of a class or kind not made in Canada	Free	15

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, October 3, 1956.

Licensing and exchange controls: None.

Import quotas: None.

Other charges: Sales tax of 10 percent of the duty-paid value. This is a general tax imposed on domestic as well as imported materials. It is not collected on materials that are consumed or expended in the manufacture of goods.

TABLE 29.—*Rates of import duty on vanadium raw materials and products into Federal Republic of Germany* [1]

Tariff No.	Form	Import duty, ad valorem, percent	Turnover-equalization tax, percent of duty-paid value
Ex. 2601 C [2]	Ores containing vanadium	Free	Free.
8108 [2]	Vanadium metal:		
	A, Crude, waste; scrap	do	4
	B, Other	do	4
Ex. 7302 H [3]	Ferrovanadium	8	4
	Vanadium chemicals:		
2841 [3]	Vanadium pentoxide (vanadic anhydride)	12	4
2879 F [3]	Vanadate, vanadinate, vanadic acid, derivatives	12	4

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

[2] May be imported into Germany without import license and exchange permit.

[3] Requires an import license. The import license carries with it release of the foreign exchange required for payment. Import quotas, if any, are not shown.

ITALY

Table 31 gives the rates of import duty on various forms of vanadium for Italy. The table indicates that various charges were made in addition to the general duty levied on incoming products.

JAPAN

Japan has been one of the more consistent importers of raw materials in iron and steel products for many years. Table 32 gives some of the import tariffs and duties applicable to vanadium, raw materials, concentrates, and semifinished products for Japan.

NORWAY

A statement of rates of import duties on various vanadium products for Norway is given in table 33.

PERU

For many years, Peru supplied practically all of the vanadium required by the United States in the form of a vanadium concentrate and ore. Although Peru has long been known as an exporter of vanadium ore and concentrate, it has specific regulations applicable to the importation of vanadium products. Table 34 gives duties applying to vanadium chemicals and vanadium metal in various forms.

TABLE 30.—*Rates of import duty on vanadium raw materials and products into France* [1]

Tariff No.	Form	Minimum rates (applied to United States, ad valorem, percent [2])
26–01 M	Metallic ores and concentrates and roasted iron pyrites: Other ores including vanadium	Free.
73–02 exH	Ferroalloys: Ferrovanadium	12
81–04	Other base metals, unwrought, or wrought, and articles thereof: Vanadium:	
	a. Unwrought; waste and scrap	20
	b. Other	30
28–28 E	Other inorganic bases and metallic oxides, hydroxides and peroxides: Vanadic pentoxide	15
28–47	Salts of metallic acids (chromates, permanganates, stannates):	
	A. Aluminates (cobalt, sodium, etc.)	30
	B. Chromates and dichromates:	
	Chromates:	
	a. Zinc	25
	b. Lead	20
	c. Other (ammonium, sodium, barium, etc.) probably including vanadium	25
	Dichromates:	
	d. Sodium	20
	e. Potassium	16
	f. Other (ammonium, etc.) probably including vanadium	20
	C. Manganates and permanganates	25
	D. Molybdates (ammonium, calcium, etc.) probably including vanadium	
	E. Vanadates (ammonium, etc.)	30
	F. Zincates (cobalt, etc.)	15
	G. Other (ferrites, ferrates, tungstates, titanates, stannates, lumbates, antimoniates, etc.)	25
28–48	Other salts and peroxysalts of inorganic acids, but not including azides:	
	A. Single and complex salts of sellenium and tellerium acids	25
	B. Other	30
28–55	Phosphides:	
	A. Of calcium	20
	B. Iron, including ferrophosphorous containing 15% or more of phosphorous	15
	C. Zinc	25
	D. Copper (including copper and copper alloys containing more than 8% of phosphorous)	25
	E. Other (cadmium, tin, etc. possibly including vanadium)	25
28–56	Carbides (silicon, boron, metallic carbides): Aluminum, chromium, molybdenum, tungsten, vanadium, tantalum, titanium	25

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

[2] General rate, 3 times the minimum.

NOTE:

Additional taxes:

Sales taxes—approximately 24 percent of c.i.f. value except vanadium waste and scrap which are exempt from sales taxes.

Item 81–04 H, b—compensatory tax of 11 percent of c.i.f. value.

Items 28–47 Bc, and f—compensatory import tax of 7 percent of c.i.f. value.

Customs stamp tax of 3 percent to total customs charges.

Imports of above products from the United States require an import license obtained by the importer in France. Dollar imports are tightly screened but are more readily granted for raw materials and plant equipment than for consumer goods.

As an exception, item 28–28 E, vanadic pentoxide, may be imported without quantitative restriction from the United States and Canada without import license.

All of listed items, except 26–01 M, 73–02 exH, and 81–04 H, a, may be imported from OEEC (Organization for European Economic Cooperation) participating countries without quantitative restrictions.

TABLE 31.—*Rates of import duty on vanadium raw materials and products into Italy*[1]

Tariff No.	Form	General	Conventional percentage ad valorem take lowest rate	Temporary
261 (m) [2]	Metallic ores: Ores of molybdenum, tungsten, vanadium, tantalum, titanium, zirconium and glucinium	Free		
315 (c) [3,4]	Oxides of tungsten (tungstic anhydride), of vanadium (vanadic anhydride), of titanium (titanium white): Vanadium oxide	10		9
324 (n) [3,4]	Chlorides:			
	Unspecified chlorides	20		13
	Ferrous and ferric chlorides		7	6
337 (o) [3,4]	Sulfates: Other (except the alums)	20		13
361 [3,4]	Other inorganic chemicals, n.e.s.	30		18
876 (h) [3]	Ferroalloys in crude state: Ferromolybdenum, containing over 5 through 90 percent of molybdenum	10		9
1004:	Vanadium (metal):			
(a) [2]	Crude oil in scrap	3		
(b) [2]	Semiworked (in bars), rods, strip, wire, tubes, and pipes and in manufactures n.e.s.	3		

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

[2] License free.

[3] Import license required (quota unknown).

[4] Compensatory import tax = 1 percent on duty and on turnover-tax (IGE) paid value.

Turnover-tax = 3 percent of duty-paid value.

TABLE 32.—*Rates of import duty on vanadium raw materials and products into Japan*[1]

Tariff No.	Form	Percent ad valorem
1401	Metal ores (including those calcined), matte, bottom, and slag (including vanadium ore and concentrate)	Free.
1405	Iron and steel, excluding special steel as specified elsewhere: 1. Lumps, ingots, blooms, billets, and slabs:	
	B. Ferromanganese and other ferroalloys	10
1423	Metals enumerated in any of the items of this group other than this item, having such forms as not specified in the item concerned, and metals not elsewhere provided for:	
	1. Lumps, ingots, slabs, grain, and powder (includes vanadium unwrought)	10
	2. Bars and rods (including those in the shape of a c 390 T, angle, etc., in section), plates, sheets, ribbons, hoops, bands, wires, pipes, tubes, wire ropes, and foils (includes vanadium wrought)	15
1718	Catalysts, containing platinum, vanadium, iron, or their compounds	Free.

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

Licensing and exchange controls: There as no quantitative quotas as such applicable to vanadium ore, concentrate, etc., into Japan, but the all-inclusive Foreign Exchange and Trade Control system in Japan has the effect of limiting imports into that country.

TABLE 33.—*Rates of import duty on vanadium raw materials and products into Norway* [1]

Form	Crowns per kilogram
Metals:	
I. Crude, in lumps, granules, blocks, and bars, as well as in sheets and the like, not having undergone any process beyond casting; old metal goods fit only for resmelting; scrap metal (probably including vanadium concentrate and vanadium metal)	Free.
III. Metals in combination with metallic oxides, sulfides, chlorides, bromides, iodides, and cyanides, alloys and amalgams, insofar as they are not classified under any other tariff item; includes ferrovanadium and probably includes vanadium oxide, vanadium chemicals, and vanadium derivatives	Do.

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

SPAIN

Spain has been a small importer of ferrovanadium and was apparently dependent upon the United States for small quantities of this alloying material. Rates for imports on various vanadium materials are given in table 35.

SWEDEN

One of the more consistent importers of vanadium oxide was Sweden. Table 36 summarizes import duties on various vanadium products.

SWITZERLAND

Switzerland maintains import duties on numerous vanadium raw materials and products, as shown in table 37.

YUGOSLAVIA

Yugoslavia had no customs tariff applicable to commercial imports. The fiscal and protective functions of tariff duties were performed by import coefficients applied to the rate of exchange.

The official commodity list of import coefficients of Yugoslavia contains no reference to any vanadium product. Normal commercial imports of vanadium products by importing or manufacturing enterprises would be subject to an effective premium of 200 percent on the normal exchange rate of 632 dinars to the dollar. In practice, an unfavorable rate of this type probably would not be applied to an essential commodity that was not produced domestically in adequate quantities. Imports would be made by a Government agency or institution at a favorable rate of 300 dinars to the dollar, or other

TABLE 34.—*Rates of import duty on vanadium raw materials and products into Peru* [1]

Tariff No.	Form	Specific duty, soles per net kilogram [2]	Specific duty, soles per gross kilogram [3]	Ad valorem surtax on c.i.f. value, percent
425	Chemical elements: Metalloids: Other metalloids not specifically mentioned	15.00		13.667
434	Metals: Other metals not specifically mentioned	2.50		13.667
471	Oxides and hydroxides: Other oxides, dioxides, peroxides, and other oxides not elsewhere specifically included		1.50	13.667
2333	Metal ores chiefly to be alloyed with iron, such as molybdenum, vanadium, tungsten, manganese, chromium, and other		.06	13.667
2337 [4]	Ferroalloys, such as ferrochromium, ferromanganese, ferromolybdenum, ferrotungsten, ferrosilicon, ferrovanadium, and other, crude		.06	12.5
2340	Ferroalloys in general, in the form of blocks, cast or rolled ingots (blooms), slabs to be rolled, or other similar forms simply rough turned or roughed down by rolling or forging and requiring to be further processed		.18	12.5
2345 [4]	Bars of iron or steel alloys of any kind and of any section, thickness, or length		.18	12.5
2354 [4]	Wire and rods of iron or steel alloys, prepared for autogenous welding and metalization		.25	12.5
2358	Bends, hoops, circles, and strips up to 20 centermeters, in width and up to 1 millimeter in thickness, of iron or steel alloys		.25	13.667
2360	Bends, hoops, circles, and strips up to 20 centermeters in width, more than 1 and up to 3 millimeters in thickness, for any use of iron or steel alloys		.25	13.667
2368	Plates, flat, of iron or steel alloys, of any shape or size, neither drilled, painted, nor varnished		.25	13.667

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

[2] Net weight is the weight of the goods, exclusive of any outer and inner packing; 1 kilogram equals 2.2046 pounds.

[3] Gross weight is the weight of the goods together with outer and inner containers; 1 kilogram equals 2.2046 pounds.

[4] Duties on these items are bound by the General Agreement on Tariffs and Trade (GATT).

favorable conditions would be applied at the discretion of the Yugoslav Government.

In a consideration of the import duties on vanadium raw materials and derivatives, the various duties in effect are, of course, im-

TABLE 35.—*Rates of import duty on vanadium raw materials and products into Spain*[1]

Tariff No.	Form	First tariff, gold pesetas [2]	Second tariff, gold pesetas [2]
57	Ores not specifically mentioned (including vanadium ore) — per metric ton gross	1.51	0.38
Ex. 256	Ferrovanadium — per 100 kilograms net	21.17	13.61
Ex. 491	Vanadium metal and concentrates — per 100 kilograms net	91.48	45.74
	Other chemical products :[3]		
975	Commercial — per 100 kilograms, net	151.20	90.72
976	Pure and pharmaceutical — per 100 kilograms net	453.60	272.16

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

[2] 1 gold peseta = $0.178.

[3] Vanadium oxide, chemicals, and derivatives are not mentioned in the Spanish tariff. They are presumably classified under items 975 or 976, according to kind.

NOTE.—All imports are subject to license by Ministry of Commerce. The internal distribution of ferrovanadium is subject to the control of COMEIM. (Regulating Council of Special Minerals of Military Interest).

TABLE 36.—*Rates of import duty on vanadium raw materials and products into Sweden*[1]

Statistical No.	Form	Crowns per 100 kilograms
414:4	V. A. Stone, earth, ores, etc.: Ores, also in briquettes: Vanadium	Free.
	XV. Nonprecious metals and manufacturers thereof:	
1338:2	A. Ferrovanadium	Do.
1579:6	B. Other nonprecious metals and manufacturers including vanadium metal	Do.
	VI. A. Chemical raw materials, etc.: Oxides, hydroxides, fluorides, etc.:	
493:3	Metal carbides, n.o.s.	Do.
501	Bromides and iodides of metals	Do.
513:2	Chromates — other	Do.
516:17	Other kinds, probably including vanadium oxide, vanadium chemicals, n.o.s., and vanadium derivatives	Do.

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

NOTE.—Metallic ores, metals, and chemicals are on the dollar import free list.

TABLE 37.—*Rates of import duty on vanadium raw materials and products into Switzerland* [1]

Tariff No.	Form	Import duty in Swiss francs per 100 kilos	Additional tare percentage	Sales tax in Swiss francs [2] per 100 kilos
Ex. 875	Vanadium ore	0.50		
Ex. 878	Metallic vanadium, crude	10.00	20	
Ex. 710 b.	Ferrochrome, ferrosilicon, ferrovanadium, and other ferroalloys, crude	.50		
	Inorganic prepared auxiliary meterials, for industrial use:			
Ex. 1048 b.	Vanadium chemicals and compounds	3.00	20	10.00

[1] Furnished by Bureau of Foreign Commerce, U.S. Department of Commerce, Oct. 3, 1956.

[2] Franc = $0.234.

portant; however, other items that could cause delay are various certificates, licenses, fees and assessments, taxes, shipping documents, quotas, and other import restrictions. Because there is no overall rule to cover importation into a particular country, each raw material, product, or derivative must be checked for specific regulations.

BIBLIOGRAPHY[16]

(Arranged in chronological order)

1. Stutzer, O. Die Eisenerzlagerstätten bei Kiruna. [Iron Ore Deposits Near Kiruna.] Ztschr. prakt. Geol., vol. 14, 1906, pp. 65–71.
2. Hewett, D. F. Vanadium Deposits in Peru. Trans. AIME, vol. 40, 1909, pp. 274–299.
3. Bayley, W. S. Iron Mines and Mining in New Jersey. New Jersey Geol. Survey, Final Rept. vol. 7, 1910.
4. De Launay, L. Traité de Métallogénie. [Treatise on Metallogeny.] Gites Mineraux et Metalliferes, Paris, France, 1911.
5. Singewald, J. T., Jr. The Titaniferous Iron Ores in the United States. Bureau of Mines Bull. 64, 1913, 145 pp.
6. Baragwanath, J. G. The Vanadiferous Asphaltites of Central Peru. Eng. Min. Jour., vol. 111, 1921, pp. 778–781.
7. Bayley, W. S., Magnetitic Ores of North Carolina—Their Origin. Econ. Geol., vol. 16, 1921, pp. 142–152.
8. Baughmann, G. W. Notes on Metallurgy of Vanadium. Trans. Am. Electrochem. Soc., vol. 43, 1923, p. 283.
9. Fox, C. S. Bauxite and Aluminous Laterite Occurrences of India. Geol. Survey India Mem., vol. 49, 1923.
10. Clarke, F. W. The Data of Geochemistry. Geol. Survey Bull. 770, 1924, 841 pp.
11. De Golyer, E. L. The Occurrence of Vanadium and Nickel in Petroleum. Econ. Geol., vol. 19, 1924, pp. 550–558.
12. Hess, F. L. Marketing of Vanadium Ores and Metals. Eng. Min. Jour., vol. 118, 1924, pp. 694–698.
13. Hallimond, A. F. Bedded Iron Ores of England and Wales. Geol. Survey England, Mem. 29, 1925.
14. Von Seth, Rutger. Über die Möglichkeiten, das Vanadin aus den Vanadinhaltigen Eisenerzen zu gewinnen. [How to Obtain Vanadium from Vanadium Containing Ores.] Metall und Erz, vol. 10, No. 22, 1925, pp. 219–222.
15. Cohen, Solomon Solis, M.D., and Githens, Thomas Stotesbury, M.D. Pharmacotherapeutics, Materia, Medica, and Drug Action. D. Appleton & Co., New York, N.Y., 1928, pp. 727–731.
16. Alexander, Jerome. Vanadium and Some of It's Industrial Applications. Jour. Soc. Chem. Ind., London, vol. 48, Sept. 6, 1929, p. 871.
17. Fersman, A. E. Geochemische Migration der Elemente, Pt. 2. Die Uran-Vanadium Grube Tuja Mujun in Turkestan. [Geochemical Migration of Elements, Part 2. Tuja Mujun Uranium-Vanadium Deposits in Turkestan.] Abh. prakt. Geologie und Bergwirtschaftslehre, Halle, vol. 19, 1930.
18. Clark, A. W. The Ore Deposits of the Otavi Mountains, Southwest Africa. Min. Mag., vol. 44, 1931, pp. 265–272.
19. Engineering and Mining Journal. Vanadium Recovery at Rhodesian Broken Hill. Vol. 131, No. 6, Mar. 23, 1931, p. 259.
20. Burwell, Blair. Mining Methods and Costs at the Vanadium Mine of the United States Vanadium Corporation, Rifle, Colo. Bureau of Mines Inf. Circ. 6662, 1932, pp. 3–7.
21. Ellsworth, H. V., and Gunning, H. C. An Occurrence of Vanadium-Bearing Rock on Quadra Island, British Columbia. Canada Geol. Survey Summary Rept., pt. A–II, 1932.
22. Jost, Konrad. Über den Vanadiumgehalt der Sedimentagesteine und sedimentaren Lagerstätten. [Vanadium Content of Sedimentary Rocks in Sedimentary Deposits.] Chemie der Erde, vol. 7, 1932, pp. 177–290.
23. Moritz, H. Die Sulfidschen Erze der Tsumeb-Mine vom Ausgehenden bis zur XVI. Neues Jahrb. der Min., supp., 67A, 1933, pp. 118–154.
24. Pavlenko, D. M. [New Data on the Geology and Genesis of the Tyuya Muyan Deposit in Uzbekistan.] Problems of Soviet Geology, Leningrad and Moscow, vol. 4, 1933, pp. 123–141.

25 Skerl, A. C. Vanadium at the Rhodesia Broken Hill. Min. Mag., vol. 50, 1934, pp. 280–283.

26. Weeks, Mary Elvira. The Discovery of the Elements. Mack Printing Co., Easton, Pa., 1934, p. 87.
27. Pickard, T. R. Recovering Zinc and Vanadium at the Rhodesia Broken Hill Plant. Eng. Min. Jour., vol. 136, No. 10, October 1935, pp. 489–493.
28. Dunn, J. A., and Dey, A. K. The Mineral Deposits of Eastern Singhbhum and Surrounding Areas. Geol. Survey India Mem. 69, pt. 1, 1937, 279 pp.
29. Peterson, N. P. Geology and Ore Deposits of the Mammoth Mining Camp Area, Pinal County, Arizona. Arizona Bur. Mines Bull. 144, Geol. ser. 11, 1938, 63 pp.
30. Zieler, H. The Production of Vanadium From German Raw Materials. Stahl u. Eisen, vol. 58, No. 28, 1938.
31. Priestly, W. J. Vanadium in Steel and Iron—A Review—Part I. Metals and Alloys, vol. 9, No. 8, August 1938, pp. 193–197.
32. ———. Vanadium in Steel and Iron—A Review—Part II. Metals and Alloys, vol. 9, No. 9, September 1938, pp. 237–241.
33. American Society for Metals. Metals Handbook. Cleveland, Ohio, 1939, pp. 594–600, 615.
34. Weyl, W. A., Pincus, A. G., and Badger, A. E. Vanadium as a Glass Colorant. Jour. Am. Ceram. Soc., vol. 22, No. 11, 1939, pp. 374–377.
35. Frankel, J. J. and Grainger, G. W. Notes on Bushveld Titaniferous Iron Ore. South African Jour. Sci., vol. 37, 1940, pp. 101–110.

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[16] Titles enclosed in brackets are translations from the language in which the item was published.

36. Frick, F. F. and Woodman, F. W. (assigned to Anaconda Co.). Recovery of Vanadium. U.S. Patent 2,193,092, Mar. 12, 1940, p. 192.

37. Assarsson, G. [The Vanadium Content of Swedish Oil Shale and the Occurrence of Vanadium.] Geol. Foren., Stockholm, Forh., vol. 63, No. 2, 1941.

38. Dawe, C. N. How Vanadium Influences Design Materials. Machine Design, vol. 13, No. 10, 1941, pp. 49–53, 110–112.

39. Diemer, R. A. Titaniferous Magnetite Deposits of the Laramie Range, Wyoming. Wyoming Geol. Survey Bull. 31, 1941, 23 pp.

40. Chemical Abstracts. Vol. 35, No. 22, May 20, 1941, p. 6106.

41. Janssen, J. J. H. (assigned to Shell Development Co.). Vanadium Recovery from Crude Oils. U.S. Patent 2,242,675, May 20, 1941.

42. Robertson, John, Dunn, H. E., and Sproul, A. A. (assigned to Vanadium Corp. of America). Extraction of Vanadium Values From Vanadium-Bearing Values. U.S. Patent 2,-257,978, Oct. 7, 1941.

43. Huttl, John B. Mammoth-St. Anthony's Complex Operations. Eng. Min. Jour., vol. 142, No. 12, December 1941, pp. 42–45.

44. Fischer, R. P. Vanadium Deposits of Colorado and Utah. Geol. Survey Bull. 1942, p. 936.

45. The Mining and Contracting Review. Vanadium. Vol. 44, No. 14, July 31, 1942, pp. 10, 12–15.

46. Engineering and Mining Journal. Vanadium from Phosphate Rock. Vol. 143, No. 10, October 1942, p. 61.

47. Mineral Trade Notes. Mar. 20, 1942, pp. 16–17, and December 1942, pp. 12–13.

48. Balsley, J. R., Jr. Vanadium-Bearing Magnetite-Ilmenite Deposits Near Lake Sanford, Essex County, N.Y. Geol. Survey Bull. 940–D, 1943, pp. 99–123.

49. Nelson, J. J. (assigned to Anaconda Co.). Recovery of Vanadium. U.S. Patent 2,357,488, Sept. 5, 1944, p. 194.

50. Schwellnus, C. M., and Willemse, J. Titanium and Vanadium in the Magnetic Iron Ores of the Bushveld Complex. Geol. Soc. South Africa, Trans., vol. 47, 1944, pp. 93–105.

51. Wood, C. E., Joseph, T. L., and Cole, S. S. Smelting of Vanadium-Bearing Titaniferous Sinter in an Experimental Blast Furnace. Bureau of Mines Rept. of Investigations 3679, 1943, 24 pp.

52. Mining World. Unusual Metallurgy—Mammoth—St. Anthony, Ltd. Vol. 6, No. 9, September 1944, pp. 23–27.

53. Allen, J. E. A Vanadium-Bearing Black-Sand Deposit of Middle Mesozoic Age in Central Curry County, Oreg. Geol. Soc. Oregon County News Letter (abs.), vol. 11, 1945, p. 21.

54. Hutton, C. O. The Ironsands of Fitzroy, New Plymouth. New Zealand Jour. Sci. and Tech., vol. 26, 1945, pp. 291–302.

55. Stephenson, R. C. Titaniferous Magnetic Deposits of Lake Sanford Area, New York. AIME Tech. Pub. 1789, Min. Technol., vol. 9, No. 1, New York State Mus. Bull. 340, 1945.

56. Joint Intelligence Objective Agency. Recovery of Vanadium From Iron and Steel Plant Slags. Rept. 23, Washington, D.C., June 30, 1945, pp. 2–4.

57. Vivian, C. H. Vanadium—A Metal Named for a Goddess. Compressed Air Mag., vol. 50, No. 10, October 1945, pp. 260–264.

58. Cole, Sanford S., Holiday, Metuchen, and Robert L., and Breitenstein, John S. (assigned to National Lead Co.). Precipitation of Hydrous Vanadium Oxide. U.S. Patent 2,479,905, Mar. 5, 1946.

59. Fischer, R. P. German Iron Ores Yield Vanadium. AIME Tech. Pub. 2070, 1946.

60. Roy, B. C. Vanadium. India Geol. Survey Records, vol. 76, No. 4, 1946, 14 pp.

61. De Mille, John B. Strategic Minerals. McGraw-Hill Book Co., Inc., New York, N.Y., 1947, p. 625.

62. Fischer, R. P., Haff, J. C., and Rominger, J. F. Vanadium Deposits Near Placerville, San Miguel County, Colorado. Colo. Sci. Soc. Proc., vol. 15, 1947, pp. 115–134.

63. Larson, C. B., and Welker, K. K. Vanadium Resources of Peru. Bureau of Mines Mineral Trade Notes, vol. 25, No. 1, Spec. Supp. 16, 1947.

64. Hewett, D. F. The Story of Mina Ragra-Premier Vanadium Find. Eng. Min. Jour., vol. 148, No. 1, January 1947, pp. 59–63.

65. Electromet, Ferro-Alloys and Metals. Electro Metallurgical Co., New York, N.Y., 1948, p. 56–57.

66. Strauss, Jerome, and Franklin, F. F. Vanadium in Steel. Metals Handbook, Am. Soc. Metals, Cleveland, Ohio, 1948, pp. 485–488.

67. Sykes, W. P. C–V Carbon-Vanadium. Metals Handbook, Am. Soc. Metals, Cleveland, Ohio, 1948, p. 1184.

68. Compagnie de Produits Chemiques et Electrometallurgique Alais. Froges & Camargue, British Patent 600,833, Apr. 20, 1948; Chem. Abs., vol. 42, p. 7225.

69. Eckel, E. B. Geology and Ore Deposits of the La Plata District, Colorado. Geol. Survey Prof. Paper 219, 1949, 179 pp.

70. Novick, David, Anshen, Melvin, and Truppner, W. C. Wartime Production Controls. Columbia Univ. Press, New York, N.Y., 1949, p. 441.

71. Russell, T. C. Mining of Phosphate Rock at Conda, Idaho, in Symposium on Western Phosphate Mining. Mining Eng., vol. 1, 1949, p. 279–282; Trans. AIME, vol. 184, 1949.

72. Staff, Natural Resources Section, General Headquarters, Supreme Commander for the Allied Powers. Japanese Natural Resources. Tokyo, Hosokawa Printing Co., 1949.

73. Asak, Ragnvald (assigned to Christiania Spigerverk, Nydalem near Oslo, Norway). Treatment of Vanadium-Bearing Ores. U.S. Patent 2,482,311, Sept. 20, 1949.

74. Bain, G. W. Geology of the Fissionable Materials. Econ. Geol., vol. 45, 1950, pp. 273–323.

75. General Services Administration. Federal Records of World War II. 1950.

76. Lovering, T. S., and Goddard, E. N. Geology and Ore Deposits of the Front Range, Colo. Geol. Survey Prof. Paper 223, 1950, 319 pp.

77. Magnusson, N. H. Världens Titanmalmstillgánger. [Titanium Resources of the World.] Teknisk Tidskrifft, Argang 80, Stockholm, Sweden, 1950.

78. Rankama, Kalvero, and Sahama, Th. G. Geochemistry. Univ. Chicago Press, Chicago, Ill., 1950.

79. Kinzel, A. B. Vanadium Metal, A New Article of Commerce. Electro Metallurgical Co. (Reprint from Metal Prog.). New York, N.Y., September 1950, 10 pp.

80. Banning, L. H., and Rasmussen, R. T. C. Processes for Recovering Vanadium From Western Phosphates. Bureau of Mines Rept. of Investigations 4822, 1951, p. 44.
81. Newhouse, W. H. and Hagner, A. F. Preliminary Report on the Titaniferous Iron Deposits of the Laramie Range, Wyoming. Geol. Survey Open-File Rept., 1951.
82. Radhakrishna, B. P., The Iron-Ore Resources of Mysore. Mysore Geol. Assoc. Bull. 2, 1951.
83. Back, A. E., Chindgren, C. J., and Peterson, R. G. Treatment of Titaniferous Magnetite Ore From Iron Mountain, Wyo. Bureau of Mines Rept. of Investigations 4902, 1952, 15 pp.
84. Fischer, R. P., and Hilpert, L. S. Geology of the Uravan Mineral Belt. Geol. Survey Bull. 988–A., 1952, 13 pp.
85. Fyfe, H. E. The Iron-Ore Resources of New Zealand. In Symposium sur les gisements de fer du monde. 19th Internat. Geol. Cong., Algiers, vol. 2, 1952, pp. 289–294.
86. Macmillan, R. T., Heindl, R., and Conley, J. E. Soda Sinter Process for Treating Low-Grade Titaniferous Ores. Bureau of Mines Rept. of Investigations 4912, 1952, 62 pp.
87. Stigzelius, Herman. Iron-Titanium Mine Starts Up in Finland. Eng. Min. Jour., vol. 153, No. 5, 1952, pp. 126–127.
88. Trefzger, E. F. Die Vanadiumlagerstätte Mina Ragra in Peru. [Mina Ragra Deposits of Vanadium in Peru.] Bei der Naturf. Gesell. zu Freiburg in Breisgau, vol. 42, 1952, pp. 211–233.
89. Perrin, T. S., Jenkins, J. N., and Banner, R. G. H. Vanadium Recovery From Chromite Liquors. Ind. Eng. Chem., vol. 44, No. 2, February 1952, pp. 401–404.
90. Perrin, T. S., and Banner, R. G. (assigned to Diamond Alkali Co.). Method of Recovering Chromates and Vanadates From Aqueous Solutions. U.S. Patent 2,628,154, Feb. 10, 1953.
91. Chemical Abstracts. Vol. 46, No. 9, May 10, 1952, p. 3924–b.
92. Rostoker, R., McPherson, D. J., and Hansen, M. Exploration of Vanadium Base Alloys, Armour Research Foundation, Illinois Inst. Technol., WADC Tech. Rept. 52–145, May 1953, p. 3.
93. Banning, L. H., and Anable, W. E. (assigned to United States of America). Tristage Crystallization and Hydrolysis for Recovering Vanadium, Phosphorus, and Chromium From Ferrophosphorus and Like Materials: U.S. Patent 2,654,655, Oct. 6, 1953.
94. Green, Jack. Geochemical Table of the Elements for 1953. Geol. Soc. Am. Bull., vol. 64, 1953, pp. 1001–1012.
95. Seybolt, Alan V. Vanadium, Modern Uses of Nonferrous Metals. AIME Ser., New York, N.Y., 1953, p. 482.
96. Shimkin, Demitri B. Minerals—A Key to Soviet Power. Harvard Univ. Press, Cambridge, Mass., 1953, pp. 90–93.
97. Steen, Charles A., Dix, George P., Jr., Hazen, Scott W., Jr., and McLellan, Russell R. Uranium-Mining Operations of the Utex Exploration Co. in the Big Indian District, San Juan County, Utah. Bureau of Mines Inf. Circ. 7669, 1953, pp. 1–13.
98. Albritton, C. C., Jr., Richards, Arthur, Brokaw, A. L., and Reinemund, J. A. Geologic Controls of Lead and Zinc Deposits in the Goodsprings (Yellow Pine) District, Nevada. Geol. Survey Bull. 1010, 1954, 111 pp.
99. Frylkund, V. O., Jr., Harner, R. S., and Kaiser, E. P. Niobium (Columbium) and Titanium at Magnet Cove and Potash Sulphur Springs, Arkansas. Geol. Survey Bull. 1015–B, 1954, pp. 23–57.
100. Goldschmidt, V. M. Geochemistry. Clarendon Press, Oxford, England, 1954.
101. Johnstone, Sidney J. Minerals for the Chemical and Allied Industries, Vanadium Chapter. John Wiley & Sons, Inc., New York, N.Y., 1954, 692 pp.
102. Kaiser, E. P., Herring, B. F., and Rabbitt, J. C. Minor Elements in Some Rocks, Ores, and Mill and Smelter Products. Geol. Survey TEI–415, issued by AEC Tech. Inf. Service, Oak Ridge, Tenn., 1954, 119 pp.
103. Parkin, L. W., and Galsson, K. R. The Geology of the Radium Hill Uranium Mine, South Australia. Econ. Geol., vol. 49, 1954, pp. 815–825.
104. World's Non-Ferrous Smelters and Refineries. Quin Press, Ltd., London, England, 1954, 432 pp.
105. Dare, W. L., Lindblom, R. A., and Soule, J. H. Uranium Mining on the Colorado Plateau. Bureau of Mines Inf. Circ. 7726, 1955, 60 pp.
106. Encyclopedia of Chemical Technology. Vanadium Compounds. Interscience Publishers, Inc., New York, N.Y., vol. 14, 1955, pp. 600–601.
107. Harki, Ilmari. Vanadium. Finnish Trade Review, 1930–55. The Finnish Foreign Trade Assoc., Helsinki, Finland, vol. 89, 1955, pp. 194–195.
108. Martin, Geoffrey, and Francis, Wilfred. Ind. Chem., Inorganic, Philosophical Library, Inc., New York, N.Y., vol. 2, 6th ed., 1955, p. 397.
109. McClintick, R. J., Bauer, G. W., and Busch, L.S. A New Titanium Alloy. Materials and Methods, vol. 42, No. 2, 1955, pp. 90–92.
110. McKelvey, V. E., Everhart, D. L., and Garrels, R. M. Origin of Uranium Deposits. In Bateman, A. M., ed. Fiftieth Anniversary Volume. Econ. Geol., pt. 1, 1955, pp. 464–533.
111. Mining Journal. Titanium and Vanadium From New Zealand Iron Sands. Vol. 245, No. 6269, 1955, pp. 436–437.
112. Robinson, S. C. Mineralogy of Uranium Deposits, Goldfields, Saskatchewan. Canada Geol. Survey Bull. 31, 1955.
113. Skinner, Walter E. Mining Year Book 1955. London, England, 1955, p. 388.
114. American Iron and Steel Institute. Steel Products Manual. Tool Steels, New York, N.Y., April 1955, pp. 5–9.
115. Glaser, Frank W. Progress Report on Cermets. Metal Prog., vol. 67, No. 4, April 1955, pp. 77–82.
116. Caldwell, Van. Beyond the Metals, Part I. Steel, vol. 137, No. 5, Aug. 1, 1955, pp. 72–74.
117. ———. Beyond the Metals, Part II. Steel, vol. 137, No. 6, Aug. 8, 1955, pp. 73–76.
118. Sherman, R. G., and Kessler, H. D. Ready—Heat-Treatable Titanium. Steel, vol. 137, No. 11, Sept. 12, 1955, pp. 98–100.
119. Bush, A. L. Vanadium-Uranium Deposits in the Entrada Sandstone, Western San Juan Mountains, Colorado. Geol. Soc. America Bull. (abs.), vol. 67, 1956, pp. 1678.

120. Crawford, John E., and Paone, James. Facts Concerning Uranium Exploration and Production. Bureau of Mines Handbook, U.S. Government Printing Office, Washington, D.C., 1956, 130 pp.

121. Finch, W. I. Uranium in Terrestrial Sedimentary Rocks in the United States Exclusive of the Colorado Plateau. In Page, L. R., Stocking, H. E., and Smith, H. B. Contributions to the Geology of Uranium and Thorium by the United States Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1955. Geol. Survey Prof. Paper 300, 1956, pp. 321–327.

122. Linares, E. The "Eva Perón" Deposit, Malargue, Mendoza. In Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, vol. 6, Geology of Uranium and Thorium. United Nations, 1956, pp. 75–81.

123. Oxford Regional Economic Atlas. The U.S.S.R. and Eastern Europe. Oxford Univ. Press, London, England, 1956, pp. 63–65.

124. Sheipline, V. M., and Runck, R. J. High Temperature Technology. John Wiley & Sons, Inc., New York, N.Y., 1956, ch. 5, Carbides, pp. 114–130.

125. Mining World. South-West Africa. Vol. 18, No. 6, May 1956, p. 72.

126. Lennemann, William L. If You're Planning Uranium Extraction, Take a Look at Today's Flowsheets. Mining Guidebook, Eng. Min. Jour., vol. 157, No. 6A, mid-June 1956, pp. 122–132.

127. Mining Congress Journal. Expands Uranium Reserves. Vol. 42, No. 11, November 1956, p. 139.

128. Ajuije, S. H. El Vanadio en el Perú. [Vanadium in Peru.] Minería (Organo del Instituto de Ingenieros de Minas del Perú), Lima, vol. 2, No. 5, 1954, pp. 19–30; No. 6, 1954, pp. 31–49; vol. 4, No. 8, 1955, pp. 21–22; No. 9, 1955, pp. 23–29. Review in English by Hugh McKinstry, Econ. Geol., vol. 52, No. 3, 1957, pp. 324–325.

129. Hodgson, G. W., and Baker, B. L. Vanadium, Nickel, and Porphyrins in Thermal Geochemistry of Petroleum. Am. Assoc. Petrol. Geol. Bull., vol. 41, pp 2413–2426.

130. Lawrence, L. J., See, G. T., McBride, Fiona, and Hofer, Hans. Davidites From the Mt. Isa-Cloncurry District, Queensland. Econ. Geol., vol. 52, 1957, pp. 140–148.

131. Lawthers, Robert. Mineralogy and Geology of Titanium Deposits. Ch. 2, In Miller, J. A., Titanium, A Materials Survey. Bureau of Mines Inf. Circ. 7791, 1957, 202 pp.

132. Robinson, S. C., Evans, H. T., Jr., Schaller, W. T., and Fahey, J. J. Nolanite, A New Iron-Vanadium Mineral from Beaver-Lodge, Saskatchewan. Am. Mineral., vol. 42, 1957, pp. 619–628.

133. Strauss, Jerome, and Cosman, C. M. Vanadium Compounds as Catalysts. The Vancoram Review. Vanadium Corp. of America, New York, N.Y., vol. 12, No. 1, 1957, pp. 16–23.

134. Verwoerd, W. J. The Mineralogy and Genesis of the Lead-Zinc-Vanadium Deposit of Abenab West in the Otavi Mountains, South-West Africa. Annanl Univ. Stallenbosch, vol. 33A, 1957, pp. 235–328.

135. Shaw, S. W. K., and Quarrel, A. G. The Formation of Carbides in Low-Carbon, Chromium-Vanadium Steels at 700° C. Jour. Iron and Steel Inst., vol. 185, pt. I, January 1957, pp. 10–22.

136. Chemical Week. Vanadium/South Africa. Vol. 80, No. 8, Feb. 23, 1957, p. 25.

137. Gurland, Joseph. Comparison of the Strength of Sintered Carbides. Jour. Metals, vol. 9, No. 4, April 1957, pp. 512–513.

138. The Wall Street Journal. Three Concerns Plan to Build South African Vanadium Mill. Vol. 149, No. 105, May 29, 1957, pp. 13.

139. Fitch, Albert J., and Herndon, John P. Anaconda's Jackpile Mine. Min. Cong. Jour., vol. 43, No. 6, June 1957, pp. 57–60.

140. The Mining Journal. Gleanings From the Reactive Metals Conference. London, vol. 248, No. 6357, June 21, 1957, p. 793.

141. Vancoram Vista. Vanadium Salts. Vanadium Corp. of America, New York, N.Y., 1957.

142. Materials in Design Engineering. Carbides. Materials Sector 1957–58 Reference Issue, vol. 46, No. 4, mid-September 1957, p. 225.

143. Society of Automotive Engineers. 1957 SAE Handbook, New York, N.Y., 1957, p. 57.

144. Rostoker, William. The Metallurgy of Vanadium. John Wiley & Sons, Inc., New York, N.Y., 1958, pp. 29–31.

145. Merrill, T. W. Ductile Vanadium a New Engineering Material. Jour. Metals, vol. 10, No. 9, September 1958, pp. 618–621.

146. Society of Automotive Engineers. 1959 SAE Handbook, New York, N.Y., 1959, p. 50.

147. Union Carbide Metals Co. Electromet Ferroalloys and Metals. February 1959, p. 27.

148. Fischer, R. P. Vanadium and Uranium in Rocks and Ore Deposits. In Garrels, R. M., and others, Geochemistry and Mineralogy of Colorado Plateau Uranium Ores. Geol. Survey Prof. Paper 320, 1959, 236 pp.

149. The Vancoram Review. Published yearly at various intervals, Vanadium Corp. of America, New York, N.Y.

150. Bureau of Mines. Minerals Yearbook and its predecessor series, Mineral Resources of the United States. Ann. pub. (Information reported in the Vanadium Chapter, 1942–59. From 1899 to 1941, vanadium information was reported regularly in a chapter reviewing several metals. Titles of the chapters varied from year to year.)

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