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Colorado

VANADIUM

A Composite Study

THE STATE OF COLORADO
METAL MINING BOARD

COLORADO VANADIUM: A COMPOSITE STUDY

STATE OF COLORADO
METAL MINING FUND BOARD

Denver, Colorado
November, 1961

To The Metal Mining Fund Board

State of Colorado

By virtue of a contract with the State of Colorado Metal Mining Fund Board of Directors, the Colorado School of Mines Research Foundation, Inc. is pleased to submit to the Metal Mining Fund Board a report entitled COLORADO VANADIUM: A COMPOSITE STUDY.

Colorado School of Mines Research Foundation, Inc. Golden, Colorado	Colorado School of Mines Golden, Colorado
E. H. Crabtree, Director	John W Vanderwilt, President
Don C. Seidel, Senior Project Engineer	Truman H. Kuhn, Dean of Faculty

November, 1961

To His Excellency, The Honorable Stephen L. R. McNichols, Governor of the State of Colorado; Dr. Edward L. Clark, Director of Natural Resources; and Members of the Forty-third General Assembly:

I have the honor to transmit the Bulletin of the Metal Mining Fund on the subject, COLORADO VANADIUM: A COMPOSITE STUDY.

Colorado State Metal Mining Fund
J. Price Briscoe, Chairman
204 State Office Building
Denver, Colorado
November, 1961

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METAL MINING FUND

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PURPOSE AND ACKNOWLEDGMENTS

Colorado vanadium production, an integral part of uranium processing, is the world's largest source of vanadium oxide (V^0S). Technological advances creating new uses and increased demands for vanadium herald the need for larger supplies and improved methods in its processing. However, because Colorado Plateau vanadium production is intimately dependent upon Atomic Energy Commission (AEC) uranium requirements, the vanadium industry has been confronted with limitations imposed by its parent activity.

Prior to 1955, rapidly expanding uranium requirements also developed the ability of Colorado mining and milling facilities to recover vanadium. Limited uses for vanadium created surpluses that were purchased and stockpiled by AEC. Newer uses and demands resulting from research have shifted the economic balance of vanadium and have stimulated industrial purchases of the material from AEC stockpiles. However, recent downpricing of uranium and a cutback in the AEC buying program threaten to reduce Colorado vanadium production because of its dependence upon the economics of uranium.

Thus, the purpose of this study is to accumulate data that give insights to the problems of vanadium production in terms of economics, reserves, metallurgy, markets, and research. Placed in the context of vanadium conservation and use, these data may form the basis for a policy directed toward an autonomous vanadium industry.

At the request of the Metal Mining Fund Board of the State of Colorado, the Colorado School of Mines Research Foundation, Inc., on December 30, 1960, entered into an agreement with the State of Colorado for the use and benefit of the State Metal Mining Fund to accumulate this information on vanadium. The results of the information (Colorado School of Mines Research Foundation, Inc., Project 800 922), conducted by Don C. Seidel and Truman H. Kuhn of the Research Foundation staff, are incorporated in this report. Although in preparing the report particular attention was paid to the vanadium industry of Colorado, it was realized that the vanadium industry of Colorado must be placed in proper perspective with other vanadium resources in the United States and other parts of the world.

Many companies and agencies were extremely generous of their time and facilities; without their help this report could not have been prepared. Personnel from Union Carbide Nuclear Company, Vanadium Corporation of America, Climax Uranium Company, Minerals Engineering Company, Chapman and Morehouse Mining Company, U. S. Bureau of

Mines, Atomic Energy Commission, and U. S. Geological Survey contributed materially in offering suggestions, supplying information, and critically discussing sections of the report. All statements in the report either are based on published accounts or are from information that has been released for publication by the company or companies having proprietary interest.

The Colorado School of Mines Library and the cooperation of the library staff have been of immeasurable assistance. Special thanks also must be given to Vanadium Corporation of America for permission to use its library at Cambridge, Ohio. With the cooperation of Union Carbide Nuclear Company and the U. S. Bureau of Mines, previously withheld figures for certain years are included in Table 1. The Denver and Washington offices of the U. S. Bureau of Mines have reviewed the data incorporated in Table 1.

SUMMARY

Vanadium production from the Colorado Plateau has been limited by the conditions of the uranium industry, its parent activity. Recent downpricing of uranium and a cutback in the Atomic Energy Commission buying program threaten to reduce Colorado vanadium output. This study is an accumulation of data that may form the basis for a policy directed toward a stable vanadium industry. Particular attention is paid to vanadium production in Colorado; however, this emphasis is balanced by placing the Colorado potential in reference to other vanadium sources in the United States and other parts of the world.

Vanadium, one of the more abundant trace elements, is widely distributed through the earth's crust. In fact, recent estimates indicate that the upper lithosphere contains on an average of 270 parts per million of VL>0.-,. Its occurrence in different types of deposits appears to be related to its chemical characteristics. A variety of vanadium minerals occurs with vanadium in oxidation states of II, III, IV, and V. Patronite. roscoelite, vanadiferous hydrous mica, carnotite, montroseite. corvusite. and vanadinite are the principal ore minerals of vanadium. By functioning in different oxidation states and forming basic as well as acidic oxides. along with the power of functioning as a central atom in polvacids, vanadium exhibits properties characteristic of the transitional metals in Group VB and the elements in Group VA.

Although commercial vanadium deposits are found in only a relatively few localities and in a relatively few types of geologic occurrences. lower-grade deposits of potential resources have been located throughout the world. Four general types of deposits account for most of the world production of vanadium: the sandstone deposits of the Colorado Plateau:

the patronite-asphaltite deposits of Minas Ragra, Peru; the vanadate deposits of Arizona, of the Otavi Mountains area of South-West Africa, and of die Broken Hill region of Northern Rhodesia; and the titaniferous magnetite deposits of Otanmaki, Finland, and Transvaal, Union of South Africa. In addition to these four general types, phosphate rocks, organic shales, certain crude oils, and manganese nodules on the ocean floor must be considered important potential resources of vanadium.

Approximately 44 percent of the world's known vanadium has come from Colorado; significantly, in 1960 Colorado ores yielded over 57 percent of the free world's vanadium oxide. Other major production in 1960 came from that portion of the Colorado Plateau in Utah, Arizona, and New Mexico (13 percent); South-West Africa (12 percent); Transvaal deposits of the Union of South Africa (9 percent) and Finland (8 percent). Between 1900 and 1945. approximately 33,640 short tons of contained VL.0.-, were mined in Colorado; between 1946 and 1960, Colorado ores yielded approximately 52,280 short tons of recoverable VL.0-,.

The first Colorado vanadium processing mill was built in 1901 near the present location of Slick Rock in San Miguel county. Between 1901 and 1961, at least 20 vanadium processing mills have been operated in the State. At present, four plants are producing vanadium from the carnotite-type ores of western Colorado.

A variety of processing techniques have been used, but most of the vanadium has been extracted by the salt-roast process, a classical method based on converting the vanadium minerals to water-soluble compounds by roasting the ground ore with salt. The vanadium is precipitated from the water-leach liquors as a polyvanadate compound, which is then dried and fused. This product, known as "fused oxide," is the basic raw material used for producing ferrovanadium. The ferro-alloy industry uses nearly 80 percent of the world vanadium. Vanadium compounds also are used as catalysts in a number of important chemical processes; for example, most of the commercial sulfuric acid production is based on converting SOo to SO3 by vanadium oxide catalysts.

Vanadium milling has passed through a number of phases in which the relative importance of the vanadium, uranium, and radium products has varied. During the past 8 years, the pace of metallurgical developments in the uranium industry has directly and indirectly influenced the processing technology of vanadium. Improved equipment for acid-circuit processing and the development of solvent-extraction separations are probably the two most significant vanadium processing innovations resulting from advances in uranium processing. Vanadium is the first nonradioactive metal processed by hydrometallurgical procedures developed for uranium production; these same procedures may be applied in milling other metals.

Irrespective of Colorado's estimated vanadium potential and impressive production history and processing developments, the industry sti faces the hard fact that vanadium continues to be recovered as a coproduct or byproduct of some other element. Consequently, intensified research and experimentation are recommended in all steps of vanadium production and processing.

HISTORY

Vanadium, a versatile element, has had a wide variety of uses ranging from grain-growth control in alloy steels to catalytic functions in manufacturing nylon and other organic compounds. In the literature on vanadium and its compounds, such descriptive adjectives as "involved," "protean," and "intricate" attest to the complexity of these substances.

Manuel delRio, a Professor of Mineralogy at the School of Mines in Mexico City, discovered vanadium in 1801. Professor delRio found the element in a lead ore and named it erythronium because the salts had the property of turning red when heated with acids. In 1805 a French chemist, Collet-Descostils, disputed delRio's discovery and stated that erythronium was nothing but impure chromium. The original discoverer accepted this premise, and it was not until 1830 that Sefstrdm rediscovered the element in Swedish iron ores. Because of its beautiful multicolored compounds, the new metal was named "vanadium" in honor of the Scandinavian goddess Vanadis. Later in 1830, Wohler published data which demonstrated that vanadium and erythronium were the same element.

A description of vanadium compounds was published by Berzelius in 1831, but it was not until the 1860's that Roscoe made extensive studies of the element and its compounds. Roscoe's work was the first to correctly place vanadium in the fifth periodic group.

Roscoe produced the first nearly pure vanadium metal when he obtained a silvery-white powder by the hydrogen reduction of vanadium dichloride (VC12). During the next 50 years many unsuccessful attempts were made to produce a high-purity vanadium metal. Because most of the products were hard, brittle crystals, vanadium was incorrectly classified in Group VA along with arsenic, antimony, and bismuth. Small amounts of impurities can have an appreciable effect upon the physical and chemical behavior of vanadium; thus, one may conjecture that a significant percentage of the early experimental work on vanadium metal and its compounds is biased by the unrecognized effects of almost trace amounts of other elements.

The first globules of ductile vanadium were produced by Marden and Rich* in 1927. These %-inch-diameter shots were made by the calcium reduction of vanadium pentoxide in a steel bomb. The product was 99.3 to 99.8 percent vanadium metal; physical-property determinations proved that the metal was not like arsenic or bismuth, but resembled tantalum.

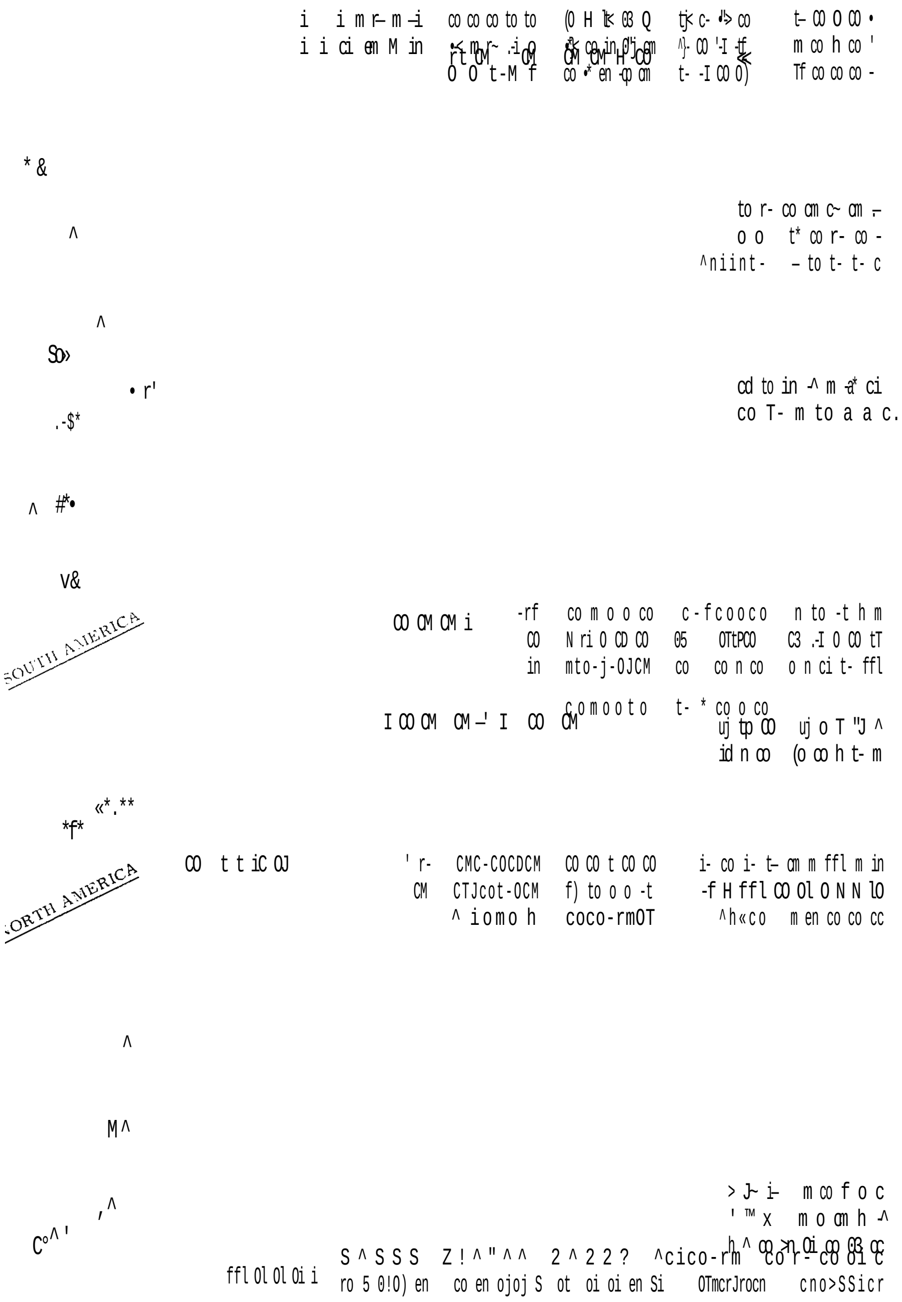
PRODUCTION

Since the first recorded production in 1900 until through 1960, approximately 44 percent of the world's known vanadium has come from Colorado and in 1960, Colorado ores yielded over 57 percent of the free world's vanadium oxide. Other major producers in 1960 included that portion of the Colorado Plateau in Utah, Arizona, and New Mexico (13 percent); the Otavi Mountains deposits of South-West Africa (12 percent); the Transvaal deposits of the Union of South Africa (9 percent) ; and the Otanmaki deposits of Finland (8 percent).

The recorded world production of vanadium pentoxide since 1900, approximately 194,500 short tons, includes vanadium recovered as a byproduct of phosphate-rock mining, but does not include vanadium recovered as a byproduct of certain other raw materials such as some iron ores, beach sands, chromium ores, furnace slags, and bauxite residue. Nor do the recorded totals include production from the U.S.S.R. and minor production from countries including Belgian Congo, Germany. Japan, Mexico, Morocco, Spain, and Norway. During World War II German production from European iron ores probably was appreciable.

Known production, given in Table 1, is graphically represented in Figure 1. Production statistics are from the yearly volumes of U. S. Department of Interior, Geological Survey, Mineral Resources of the United States;- U. S. Department of Commerce, Bureau of Mines, Mineral Resources of the United States;3 U. S. Department of Commerce, Bureau of Mines, Minerals Yearbook;4 and U. S. Department of Interior. Bureau of Mines, Minerals Yearbook/'

Vanadium production has not been reported consistently; thus for the years 1900-1945 the figures given in Table 1 represent the amount of V20.-, contained in ores and concentrates mined, shipped, sold, and received at mills. For 1946-1960 the production statistics reported in Minerals Yearbooks (1955-1960) refer to short tons of VnO.-, recovered or recoverable from ores and concentrates mined, shipped, sold, and received at mills. Consequently the figures for 1946 to 1960 are not strictly comparable with those for preceding years. An indication of the magnitude of metallurgical and other losses is given in Table 2 adopted from United States production statistics in Minerals Yearbooks for 1959 and 1960.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COLORADO VANADIUM

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TABLE 2

SHORT TONS OF V,0B PRODUCED IN THE UNITED STATES

	1950-54 Average	1955	1956	1957	1958	1959	1960
Contained in ores and concentrates	6,775	10,124	10,205	13,080	12,224	14,367	15,752
Recovered or recoverable from ores and concentrates	4,432	5,882	6,922	6,607	5,424	6,657	8,898
Ratio recoverable contained	65%	58%	68%	51%	44%	46%,	56%

Available production figures are difficult to correlate because of differences in reporting, both by the various companies and by the U. S. Bureau of Mines. Production up to 1945 was reported in terms of vanadium contained in ores or concentrates that were either mined, shipped, sold, or received at mills. It is evident that tons of contained vanadium pentoxide does not necessarily present a true picture of the amount of vanadium that found its way into industrial uses. For companies recovering vanadium, losses were experienced at each stage of the operation. Because of low grade or other unfavorable economic conditions, some processing plants made no attempt to recover vanadium sent to their plants.

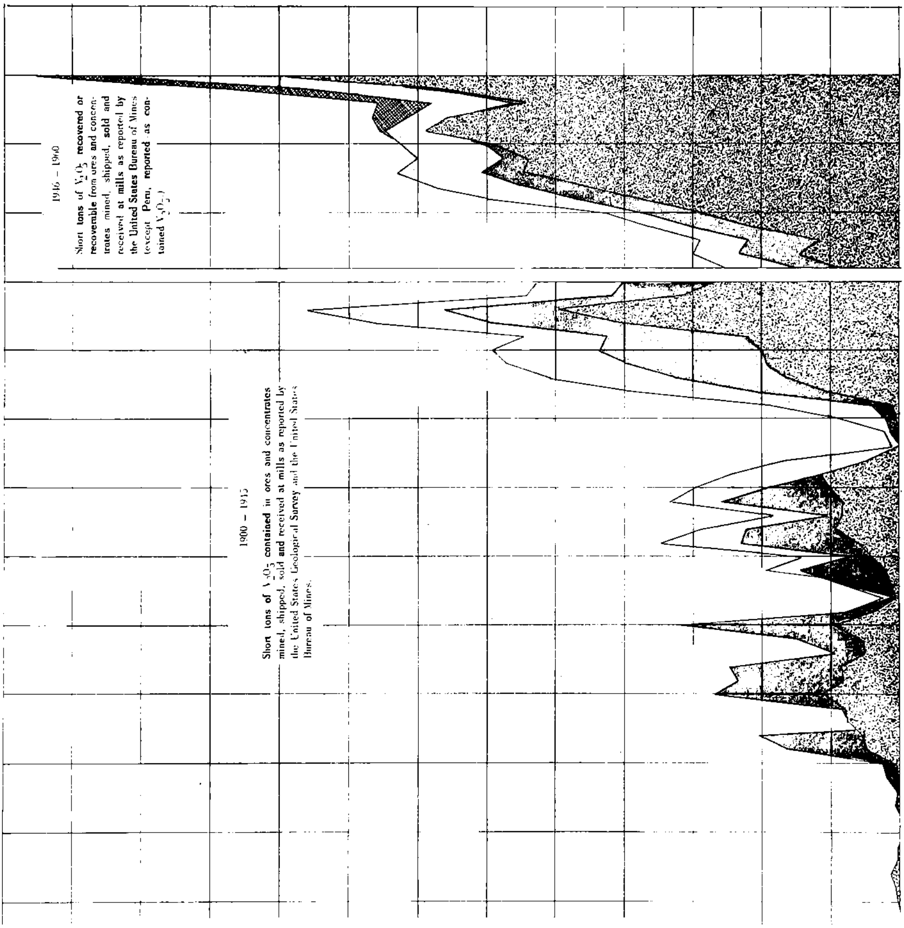
Since 1946, the U. S. Bureau of Mines reports recovered or recoverable vanadium, and these yearly figures are probably more realistic than earlier production figures.

An attempt was made to account for discrepancies of reporting and

TABLE 3

Year	U.S.B.M.	Minerals Engineering Co.	Year	U.S.B.M.	Minerals Engineering Co.
1910	251	261	1927	2,883	2,006
1911	1,613	980	1928	1,810	1,236
1912	2,053	1,404	1929	3,338	1,940
1913	773	540	1930	2,960	1,544
1914	816	529	1931	2,433	1,095
1915	2,706	1,723	1932	1,689	1,182
1916	2,346	1,589	1933	112	77
1917	2,481	1,758	1934	242	199
1918	954	823	1935	906	641
1919	1,498	1,064	1936	1,920	1,376
1920	3,229	2,347	1937	3 R-«	2,996
1921.	744				3,623
1922	187				3,984
1923	811				4,771
1924	1,943				3,861
1925	1,432				5.234
1926	3 457	2,414	1943	8,634	5,923

COLORADO VANADIUM



treatment losses. Based on adjusted figures supplied by Minerals Engineering Company (personal communication), the world production from 1910 to 1943 as obtained from Bureau of Mines publications is contrasted in Table 3 with figures adjusted to compensate, in part, for treatment losses and for differences in methods of reporting.

The world production figures for 1910 through 1943 adjusted by Minerals Engineering Company to compensate for differences in reporting and for treatment losses total about 69 percent of tonnage reported by the Bureau of Mines (Table 1). This figure is somewhat higher than the average 57 percent ratio of contained to recoverable vanadium in United States production as reported by the Bureau of Mines for 1950 through 1960 (Table 2).

The supply of vanadium became plentiful with the discovery of the rich vanadium deposit at Minas Ragra, Peru, in 1905; production of four tons was noted in 1907. This output increased to 1,121 tons in 1911, with a maximum production of 2,286 short tons of V_2O_5 in 1920. Total production from the Minas Ragra deposit, as recorded by the U. S. Bureau of Mines, amounted to 43,000 short tons of contained V_2O_5. During the same period, 1907 through 1955, Colorado ores contained approximately 57,700 short tons of V_2O_5.

Colorado's yearly vanadium production is shown in Table 1. Except for only a few years, production from Colorado has been significant. From 1900 through 1945 approximately 33,640 short tons of contained V_2O_5 was mined in Colorado — about one-third of the world's total. From 1946 through 1960 ores from the Colorado Plateau in Colorado yielded about 55 percent of the world's recoverable vanadium pentoxide, approximately 52,280 tons.

Since about 1915 approximately 9,700 tons of V_2O_5 has been produced from the Colorado Plateau in Utah. The figure includes about 500 tons of contained V_2O_5 mined between 1915 and 1941, but because of the limited number of producers, the U. S. Bureau of Mines has not released yearly production figures. These 500 tons are included in Table 1 mainly under "Arizona and Other States," but a few tons are included in the Colorado total.

In addition to some Utah production, also included under "Arizona and Other States,'' is Colorado Plateau production from Arizona and New Mexico; vanadate production from Arizona, New Mexico, and Nevada; vanadium recovered from phosphate rock of Idaho and Montana; and sandstone production from South Dakota and Wyoming.

Several factors relating to world production are of particular interest. The United States and South-West Africa output continues to be strong. Production from Peru and Northern Rhodesia has declined and for the past several years im vanadium-bearing ores have been produced. Finland and the Union of South Africa, starting production only four or five years ago, already have reached the status of major producers.

The Colorado Plateau area of Colorado, Utah, Arizona, and New Mexico has had recorded production since 1900. Fluctuations have occurred, but, in general, production from this area has gradually increased to 1960, the peak \ear, when Plateau ores yielded o.398 short tons of recoverable V2O.-,, 7,206 tons from Colorado and 1,692 tons from the rest of the Plateau. The vanadate deposits of the Otavi Mountains of South-West Africa have not yielded as much V203 as have the Colorado Plateau ores, but the production has been consistently important, approximate!;, 15 percent of the world's total. As in Colorado, 1960 was a peak year for South-West Africa when 1,502 short tons of recoverable VjO:, was produced.

Two deposits, the extremely rich patronite deposit of Minas Ragra. Peru, and the Broken Hill, Northern Rhodesia, vanadate deposits, appear to be essentially depleted of reserves. No production has been recorded from either of these two areas since 1955. From 1907 through 1955, ores from the Minas Ragra deposit yielded 43,000 short tons of contained V^O.-j, about 22 percent of the world's known production. In a shorter period, 1922 through 1955, 10,101 short tons of V20.-, was mined in Northern Rhodesia. Northern Rhodesia has accounted for about 5 percent of the world's vanadium.

In recent years ores from two titaniferous magnetite deposits have yielded appreciable amounts of vanadium. The Otanmaki deposit in Finland began production in 1956, and 985 short tons of V20.-, were recovered in 1960 along with titanium and iron. First recorded production from the Transvaal, Union of South Africa, was in 1957. In 1960 these Transvaal ores yielded 1,110 short tons of V20.-,.

In 1960 an all-time high for the world was reached when ores and concentrates yielded a total of approximate!) 12,500 short ton of VjO-.

DISTRIBUTION

An element with an exceedingly complex chemistry, vanadium is a common constituent of the earth's crust occurring in all types of geologic environments. Average concentrations as generalized by different investigators are shown in Table 4.

In 1954 the U. S. Geological Survey published ° the results of a search for certain strategic and minor elements, including vanadium, in domestic rocks, ores, concentrates, tailings, smelter slags, and flue dusts. Spectrographic vanadium determinations were made on 778 samples. In discussing the data contained in the report, Fischer 7 concluded that the vanadium content of most samples possibly represents the vanadium content of the host rock and that vanadium does not tend to concentrate in the deposits sampled. A summary of the study also has been presented by Williamson.8

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MINERALOGY

A wide variety of vanadium minerals is found in nature with vanadium in oxidation states of II, III, IV, and V. Patronite, roscoelite, vanadiferous hydrous mica, carnotite, montroseite, corvusite, and vanadinite are the principal ore minerals of vanadium; however, even in a single deposit a wide variety of other vanadiferous minerals can be expected.

In addition to true mineral species, vanadium occurs as a replacement in magnetite, spinels, colusite, and other minerals. It is present also in petroleum and asphalt deposits probably in part only as a porphyrin.

Vanadium minerals are well described in the literature; the following descriptions (Table 5) have been taken from several sources, principally Weeks and Thompson;10 Franklin;17 ls Dunn and Edlund;10 20 and Palache, Berman, and Frondel.212- Information relating to vanadium and uranium mineralogy has been expanding very rapidly. Although all known vanadium-bearing minerals are not included in Table 5, the more important ones are described. Optical properties of most of the minerals can be found in the references listed in Table 5.

Chemical Tests for Vanadium

Weeks and Thompson 10 give the following test for vanadium: "'. . . dissolve a small part of the mineral or ore in aqua regia, evaporate to dryness, add as much water as original acid, and then add a few drops of hydrogen peroxide. If vanadium is present the solution will turn orange red.''

A field test for vanadium in soils and rocks is given in U. S. Geological Survey Bulletin 1152 -:!:

1. Fuse 0.1 gram soil or rock with 0.5 gram potassium pyrosulfate in 16 x 150 millimeter test tube.
2. Digest with 3 milliliter 1:1 hydrochloric acid or 3 milliliter (1:3) nitric acid.
3. Dilute to 10 milliliter and mix.
4. Transfer 1 milliliter to 16 x 150 millimeter culture tube.
5. Add 1 milliliter concentrated nitric acid and boil 5 seconds.
6. Add 0.3 milliliter H3P04 (85%) then 0.2 milliliter 5C{ sodium tungstate.
7. Dilute to 10 milliliter with water.
8. Place in boiling water bath for 10 minutes.
9. Compare with a standard series.

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A standard series may be prepared by adding 0, 4, 8, 15, 30, and 60 micrograms of vanadium to culture tubes, then proceeding from Step 4 above.

A standard solution of 1,000 micrograms of vanadium per milliliter is prepared by dissolving 1.785 grams of pure V203 (previously ignited) in a slight excess of NaOH, then adding slight excess of H0SO4, and dilute to 1 liter.

GEOCHEMISTRY

This discussion partly based on the expressions of Fischer,' Williamson,[8] Rankama and Sahama,[10] Goldschmidt,[15] and Pearson,[24] is limited because of the relative complexity of the chemistry of vanadium and vanadium compounds.

Vanadium, atomic number 23, is in Group VB of the Periodic Table with niobium (columbium) and tantalum. Its atomic weight of 50.95 places it horizontally between titanium and chromium; its reactivity is reported to be a mean between that of titanium and chromium. By functioning in different oxidation states and forming basic as well as acidic oxides, together with the power of functioning as a central atom in polyacids, vanadium exhibits properties characteristic of the transitional metals in Group VB and the elements in Group VA, such as phosphorus.

Major factors, when considering the complex mineralogy of vanadium and the chemical and metallurgical processing of its ores and products, are:

1. the ability of vanadium to exist in 5 oxidation states
2. the amphoteric nature of vanadium (predominately basic in the lower oxidation states, acidic in the higher)
3. its ability to form several radicals
4. its ability to enter into a great variety of complex compounds by way of its polyacids.

One of the more abundant trace elements, vanadium (II, III, IV, and V), is widely distributed through the earth's crust. Its occurrence in the different types of deposits appears to be related, in part, to its chemical characteristics.

Although reported as being identified in the laboratory, vanadium (I), which is extremely unstable, has not been found in naturally occurring compounds in the upper lithosphere.

Commercial deposits of vanadium occur only in a relatively few localities in the world, and in only a relatively few types of geologic occurrences. However, lower-grade deposits of potential resources have rather widespread worldwide occurrences.

Four general types of deposits account for the bulk of the world's production of vanadium: the sandstone deposits of the Colorado Plateau: the patronite-asphaltite deposits of Minas Ragra, Peru; the vanadate deposits of Arizona, the Otavi Mountains area of South-West Africa, and the Broken Hill region of Northern Rhodesia; and the titaniferous magnetite deposits of Otanmiiki, Finland, and Transvaal, Union of South Africa. In addition to lower-grade sandstone, asphaltite, vanadate, and titaniferous magnetite deposits; phosphate rocks, organic shales, certain crude oils, and manganese nodules on the ocean floor -•' must be considered as important potential resources of vanadium.

Goldschmidtlo pointed out the widespread occurrence of vanadium and estimated that the upper lithosphere contains on an average of 150 parts per million of vanadium (270 ppm VoO.-,). He noted that the geochemistry of vanadium is characterized by four main factors:

1. concentration of vanadium in the sulfide phase (troilite) of iron meteorites, presumably as vanadium (II) sulfide, VS. The average vanadium content for meteorites was estimated at 100 parts per million, with some of the troilite containing as much as 1500 parts per million.
2. the distribution of vanadium(III) in magmatic rocks of the upper lithosphere essentially in oxygen compounds.
3. the accumulation of vanadium, perhaps especially vanadium(IVI. in bituminous sediments.
4. the oxidation of vanadium to the pentavalent state in the cycle of weathering and sedimentation.

A constituent of all types of rocks in the earth's crust, vanadium concentrations more commonly are found associated with titaniferous magnetite deposits in magmatic rocks, in bituminous or organic sediments, in phosphate- and iron-rich sediments, and in certain sandstone deposits.

During weathering of vanadium compounds, vanadium is oxidized to the soluble vanadate ion which is able to travel in solution over a wide range of acidity or alkalinity. Vanadate ions, resulting from weathering, are able to migrate with circulating solutions either in soils or through porous rock until precipitated as a relatively insoluble vanadium compound or until solutions are evaporated.

Precipitation can be brought about by:

1. the presence of a reducing agent such as organic matter in soils or sediments, or by hydrogen sulfide.
2. local concentrations of cations of divalent lead, zinc, or copper which may form insoluble compounds with vanadium anions.
3. the precipitation of vanadate ions in the presence of divalent uranyl cations.

4. local precipitation of soluble vanadium ions by hydroxides of aluminum or of ferric iron. This process gives rise to concentrations of vanadium in residual iron ores and in certain types of bauxites, especially those rich in iron.

In general, vanadium(V) will concentrate in ferruginous zones in soils, whereas vanadium (III) concentrates in the clay fraction. Possibly some vanadate ions may be fixed to the surface of clay particles.

Residual sediments, because normally derived from vanadium-poor sources and because during weathering most of the vanadium has been removed as soluble vanadate ion, are generally lower in vanadium than the average of the upper lithosphere.

Considerable work has been done on vanadium since its discovery in 1801. However, much of the knowledge of vanadium and uranium geochemistry has accumulated since about 1950. Many of the more recent investigations relate particularly to the vanadium-bearing deposits in sandstones of the Colorado Plateau. The geochemistry of vanadium as relating to these deposits is considered in more detail in the discussion on Colorado Plateau deposits on pages 34 to 41.

DEPOSITS

The most important vanadium-bearing deposits occur in magmatic rocks associated with bodies of titaniferous magnetite; in sedimentary rocks, most commonly sandstones and shales with a high organic or phosphatic content; and in oxidized cappings of massive sulfide bodies. Characteristics of the more important deposits are discussed in relation to reserves and resources on pages 56 to 64.

Magmatic Rocks

In magmatic rocks vanadium is found most abundantly in magnetite or in the magnetite component of titaniferous magnetite deposits. In magnetic separates, at least 3 to 5 times as much vanadium is in the magnetite fraction as in the titanium-rich fraction. Vanadium in these rocks is present dominantly in the trivalent state. The vanadium content of magnetite ores from gabbroid magmas is an important potential source of vanadium.

Although vanadium minerals have been identified in hydrothermal vein deposits, hydrothermal origin for vanadium has not been definitely shown.

From the Kekionga claim, Boulder County, Colorado, Lovering and Goddard26 reported that vanadium was associated with gold tellurides in small lenticular masses ranging in width from 1 to 8 inches, in depth up to 100 feet, with a strike length up to 30 feet. In 1910 some ore was shipped for its vanadium content. The ore mineral probably was roscoelite. Some of the ore contained as much as 6.82 percent V205, and a moderate tonnage was blocked out which averaged 2 percent V205. The vanadium-bearing zone 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 samples was 4.3 percent V20.-,. Included in the composite sample was a carload of 20 tons of vanadium ore.

Galbraith,-'7 reported the widespread association of green roscoelite with gold telluride minerals in vein deposits in the La Plata district, Colorado. The roscoelite commonly occurred in small quantities in microscopic intergrowths, imparting dull green to the intergrowth. Roscoelite was more abundant in the Durango Girl mine than in any of the other mines of the district.

According to Stinson 2S some of the gold quartz veins of the Mother Lode in Amador and Calaveras Counties in California contained roscoelite. Roscoelite also was reported to be present in some of the gold telluride deposits of Kalgoolie, Australia.

Titaniferous Magnetite Deposits of Wyoming

Bodies of titaniferous magnetite on and near Iron Mountain, Albany County, Wyoming, approximately 40 miles northeast of Laramie, Wyoming, are potential sources of vanadium.29 30 Because of complex mineral associations and difficult metallurgy, there is no current vanadium production from these deposits.

Lenses and tabular bodies of the titaniferous magnetite form a dike-like zone, dipping 45° to 60°, which is associated with large anorthosite masses. The magnetite-anorthosite masses appear to intrude the central zone of the Laramie Range, a Precambrian metamorphic complex of gneiss, schist, quartzite, and marble. Surface methods could be used for all mining.

Titaniferous Magnetite Deposits of New York

Four deposits of vanadium-bearing magnetite-ilmenite ores are being mined, principally for titanium at the head of the Hudson River, near Tahawas, Lake Sanford area, Essex County, New York.30 31 The anorthosite, gabbro, and magnetite-ilmenite rocks, forming a gradational series, appear to be related to the same regional intrusion of magma. The ore consists of intermixed ilmenite, magnetite, and silicate minerals. The amount of metallic minerals range from a few percent of disseminated magnetite-ilmenite in the gabbro to over 75 percent of the rock in the richer ores. The gabbro and lean ores are a fine-grained rock composed of small crystals of feldspar and ferromagnesium minerals. The rich ore (over 75 percent metallic minerals) is a very heavy, coarse-grained rock containing up to about 25 percent biotite and large crystals of andesine.

The vanadium is in the magnetite, possibly in chemical combination with the iron of the magnetite and possibly in part included in the magnetite as very fine-grained coulsonite, an iron-vanadium oxide.

Titaniferous Magnetite Deposits of Finland

Important iron-titanium-vanadium deposits are found at Otanmaki, almost at the geographic center of Finland, approximately 300 miles north of Helsinki.[32, 33] Ore occurs in nearly vertical lenses in a zone about two kilometers long. The largest lenses are reported to be about 300 meters long, with a mining width averaging from 4 to 20 meters. A depth of 550 meters has been estimated.

The principal minerals, magnetite and ilmenite. occur as discrete grains, easily separable in the concentration process. Magnetite and ilmenite particles range in size from 0.1 to 2 millimeters with the vanadium associated with the magnetite. The main gangue minerals are chlorite, hornblende, and basic plagioclase. Chlorite is a gangue mineral in the high-grade ore; the low-grade ore contains hornblende, chlorite, and feldspar. A continuous sequence exists from ore to hornblende schist.

Titaniferous Magnetite Deposits of the Union of South Africa

A very large potential source of vanadium in the Union of South Africa is the vanadium-bearing titaniferous magnetite deposits of the Bushveld Complex in the Transvaal.[34] :S Production from this source began in 1957 with an output of 14 tons of V2Os. In 1960 ores mined from the Bushveld Complex contained 1,110 short tons of recoverable V2Or,

A saucer-shaped mass of igneous rock, the Bushveld Complex is roughly one hundred miles in diameter and covers an area of about 12,000 square miles. Several horizons of titaniferous magnetite occur in the Complex. The vanadium content of these layers, which are as much as several feet thick and continuous for miles along the outcrop, ranges up to 1.5 percent V205.

Sedimentary Rocks

Although found in all types of sedimentary rocks, vanadium is more abundantly associated with bituminous sediments, organic shales, phosphate- and iron-rich sediments, and certain sandstone deposits.

Bituminous Sediments

Vanadium is a common constitutent of bituminous sediments.

The raw oil shales of the Mahogany zone of the Green River formation in the vicinity of Rifle, Colorado, are reported to contain a maximum of 0.1 percent vanadium pentoxide. The ash from 6 selected Colorado oil shales, as determined on raw shale, ranged from 0.003 to 0.06 percent

V20-, with an average of 0.02 percent V20,-,.:;,; Subsequent work by the LI. S. Bureau of Mines on 10 additional samples from the Uinta Basin and the Piceance Creek Basin, as reported by U. S. Bureau of Mines Laramie Petroleum Research Center in a personal communication, showed a content of 0.002 to 0.02 percent V20.-,. These 10 composite samples represented the oil-shale intervals of the Mahogany zone which averaged about 25 gallons of oil per ton of shale. Vanadium also is present in the oil-shale deposits of Sweden; those in Estonia contain only a trace of vanadium.

A potentially important vanadium-bearing asphalt deposit occurs near Temple Mountain. Utah, and others are known to exist in Nevada. In the Pifion Range of Eureka County, Nevada, asphaltite containing up to one percent V20.-, occurs as cementing material in a shear zone and in bedding planes of the shale and sandstone country rock.3' Deposits of a vanadium-bearing native bitumen, grahamite, have been found enclosed in highly tilted folds in Oklahoma and Arkansas; the vein material contains from 0.1 to 0.3 percent V20.-,.',N The gilsonite deposits of eastern Utah contain minor amounts of vanadium.

A minor but important source of vanadium in the past has been the soot, ash, and refinery residues from some crude oils, especially those of Venezuela, Mexico, and Iraq. The ash of some coals contains several percent V0O5 and under favorable conditions may be potential sources of vanadium.

Asphaltite Deposits of Peru

Approximately 22 percent of the world's vanadium has come from essentially one deposit in Peru: the patronite (vanadium sulfide) deposit at Minas Ragra, near Ricran, Department of Junin.30 Quisqueite. patronite, bravoite (iron-nickel sulfide), vanadates, and vanadium oxides occupy a fracture and permeate the adjoining shales and thin-bedded limestones of Cretaceous age. The fracture dips steeply and crosses the bedding at a moderate angle.

Hewett40 excellently described the Minas Ragra deposit, but little new material regarding the deposit appeared until 1954-55 when, in a series of papers in Spanish, Aquije 41 discussed more recent information revealed by deeper mining. McKinstry's 42 English review of Aquije's article is important because it calls attention to a recent source of information regarding the Peruvian vanadium deposits:

> "The earlier papers of the series are concerned with the vanadium bearing asphaltite deposits that are so widely distributed through the Peruvian Andes. These deposits consist of fissures, or, in some cases, openings between beds, mostly of Lower Cretaceous limestone, filled with asphaltite whose content

in V ranges from 0.3 to l/< or more in places. On burning, the V remain in the ash; in general the lower the percentage of ash the higher its V content which reaches 54% in the richest sample cited.

"The Minasragra deposit although quite different from the asphaltites and much richer is linked to them by the common association of vanadium with carbonaceous material and by structural form. Contrary to some descriptions, it is fissure-like and transects the enclosing beds of red shale. The author distinguishes clearly between the primary deposit and the products of supergene alteration.

"The primary deposit has the form of a wedge or an inverted cone, elongated in plan, zoned in such a manner that the outer portion adjoining the walls is quisqueite. a lustrous hydrocarbon, within which is natural coke enveloping central shoots of patronite, a vanadium sulfide of doubtful composition. At the surface the cone was lenticular in plan, measuring 350 x 28 feet. Downward it diminished in size until at the 200 level the 'coke' had entirely disappeared; the patronite-bearing area was much reduced in size and diluted by material called Seta madre' (to be described later). The quisqueite continued and in one place extended as a tail to 40 feel below the 300 level or a depth of 253 feet below the surface.

"This main body of ore and carbonaceous matter lies within an envelope of 'bronce,' consisting of shale impregnated with vanadium sulphide and some quisqueite. The bronce grades outward from dark gray shale through gray to brown shale into the surrounding red shale of the country. At the surface it occupies an area 850 x 180 feet, diminishing at depth to a vertex at about 300 feet.

"The secondary mineralization results from weathering whereby vanadium sulphide has behaved much as would copper sulphide except that the minerals reprecipitated at depth were vanadates and vanadium oxides instead of sulphides. With depth, gypsum, derived from reaction of sulphuric acid with calcareous rocks, increases in amount and the supergene vanadium minerals are species increasingly soluble in sulphuric acid. Successive depth-zones are described as follows:

"Upper 20 feet: Vanadates and oxides, red blue, green and yellow but chiefly red and gray. Area 580 x 100 feet.

"Next 46 feet: Oxides and vanadates, chiefly green.

"Lower 167 feet: Oxides and vanadates dark green or
gray. Gypsum is abundant. Maximum area 377
x 82 feet.

The material of this deepest zone is what is called 'veta madre.'

"In its palmy days, the orebody yielded many thousand tons of a shipping product grading better than 6% V and by 1934 after nearly a quarter of a century of operation the reserves were estimated by W. Spencer Hutchinson as containing 70 million pounds of vanadium [approximately 60,000 tons V20.-j]. All that is left now of this fabulous deposit is a hole 850 x 380 feet in area and 210 feet deep with the remnant of a vein which, according to the author, does not exceed 10,000 tons of 1.75% V content. [About 300 short tons of contained V20.-,.]

"The July, 1955 installment of the paper contains half a dozen plans and sections of Minasragra drawn to scale.

"As a matter of fact, although there are a number of intrusive bodies in the neighborhood it seems improbable that the vanadium was derived from them, as the numerous hydrothermal silver-base metal deposits associated with similar intrusives in the region are notably poor in vanadium minerals even in zones of oxidized lead ores. On the contrary, the association of vanadium with carbonaceous material points to a source in common with the asphaltites and suggests that Minasragra is an oversized and modified asphaltite deposit. Driving off the volatiles, presumably by the heat of intrusives, would account for coking of the material and thus accomplish some concentration of vanadium. The segregation of patronite in the center of the body remains to be explained."

Asphaltite Deposits of Argentina

The asphaltites or solid bitumens of Argentina are irregularly distributed in a 20,000-square-mile area extending from Rio Diamente, Province of Cordoba, southward approximately 280 miles to Rio Agrio, Province of San Luis (approximately between latitudes 34° South and 38° South). The deposits are in the form of seams, veins, or irregularly shaped lenses in strata ranging in age from Middle Jurassic to Upper Cretaceous. There is no definite stratigraphic horizon.

In Mendoza Province occurrences are all of the bedded-vein type which may parallel or cut across the strata or have very irregular structural relationships. In Neuqueri Territory fracture filling and fissure-vein types are more prevalent.

Average and fairly representative analyses of asphaltites from two of the largest properties in Mendoza are given by Kett.4:!

	La Valenciono, Mendoza	Minacor, Mendoza
Number of Samples	21	21
Percent V20, in Original Material	0.217	0.204
Percent Ash	1.50	1.25
Percent V203 in Ash	14.51	16.25

Organic Shales in the Western United States

In western United States, four shale units are known whose metal content approaches ore grade.3' 44 4'' 4C

The "vanadiferous shale" in the Permian Phosphoria formation of western Wyoming and southwestern Idaho is the best known of these shale units. Less well known metalliferous shales are in the Comus formation of Ordivician age near Golconda, Nevada; in an unnamed Lower Paleozoic formation in the Fish Creek Range near Eureka, Nevada; and in the Mississippian Deseret limestone at Mercur Dome near Tintic. Utah. These shales are black and rich in organic material. The vanadium content is nearly constant along beds. The metallic elements probably occur either in metal-organic compounds or in finely dispersed sulfides.

Samples taken from these rocks contain as much as 1.5 percent zinc, 5 percent vanadium, 1 to 2 percent nickel, 0.7 percent selenium, and lesser amounts of other metals. The metal content of these black shales is higher than in the "average" shale, but the content is not much higher than that reported from some samples of Pacific palagic sediments.

The Permian Phosphoria formation and its stratigraphic equivalents crop out in Idaho, Montana, Wyoming, Utah, and the extreme northwestern corner of Colorado.47 Two facies are recognized. The western facies is characterized by a complex geologic structure and by black shales, cherts, carbonaceous mudstones, and black phosphorites. The eastern facies, a region of simple geologic structure, has a predominance of carbonate rocks with interbedded layers of chert, sand, limestone, and low-grade phosphatic rock. Vanadium apparently is more abundant in the western facies, particularly in southeastern Idaho and western Wyoming associated with carbonaceous mudstone. The irregular boundary between the two facies roughly approximates meridian 111°.

Within the phosphatic shale member, a member 100 to 150 feet thick and composed mainly of black shales, the individual beds are thin. ranging up to a few inches in thickness. The individual beds are widespread, and each has a nearly constant vanadium content. A two-to-ten-foot zone, about 35 to 50 feet below the top of the phosphatic member. contains the greatest concentration of vanadium, greater than that contained in the higher grade phosphate ores found in the same Phosphoria formation. A few thin central beds contain as much as 1.5 to 2.5 percent V203. The entire zone averages from 0.7 to 1.0 percent V20,-,- The beds in this zone also contain 0.02 to 0.1 percent molybdenum, 0.02 to 0.3 percent nickel, and about 0.02 percent selenium.

Phosphate-, Iron-, and Aluminum-Rich Sediments

The vanadate ion along with the phosphate ion is concentrated in sediments rich in iron. Vanadium also is commonly found in bauxite deposits.

Phosphate Deposits of Idaho, Montana, Wyoming, and Utah

Within the Permian Phosphoria formation of Idaho, Montana, Wyoming, and Utah are extensive deposits of phosphate rock48 estimated to exceed several billion tons. The phosphate ores contain up to 0.3 percent V20,-,. During treatment of the ores the small vanadium content of the rock is concentrated in the ferrophosphorous byproduct of the phosphorous smelting.40

At one producing area (the Conda phosphate mine, eight miles north of Soda Springs, Caribou County. Idaho) the main phosphate bed, "'the footwall bed," averages 7.1 feet in thickness and contains 32 percent P20.-, and 0.28 percent of V20.-,. The upper or "hanging-wall bed" averages 7.2 feet in thickness, and the analyses average approximately 30.5 percent P205 and 0.11 percent V20,.30 ",1

For a more detailed description of the phosphate-bearing rocks in the United States, reference is made to two important bibliographies—one by Harris "- and the other by Curtis."'3

Sedimentary Deposits of Western Europe

The vanadium content of marine iron sediments and the vanadium content of certain bauxite ores provide another source of low-grade vanadium.

Vanadium is present in the minette iron ores of Eastern France.1* Although production has been very limited, the French operations are of historic interest. The presence of vanadium in bauxite deposits was first reported in 1859. A short time later vanadium was recognized as having a wide distribution in the minette iron ores, and it was extracted from slags derived from the smelting of these ores. The minette ores contain amounts ranging from 0.1 to 2.0 percent V20.-,. It was estimated that about 100 tons of V20.-, were contained in slags made in one year at Le Creusot. These slags were the largest source of vanadium then known, and production was carried on until 1885, when there was no longer the demand for anilene black.

During World War II Germany recovered considerable vanadium from sedimentary iron ores containing from 0.02 to 0.2 percent V-.03.

Sandstone Deposits

The average sandstone deposit in the earth's crust has a low vanadium content, 10 to 60 parts per million (15-100 ppm V20,l. Of the geologic environments listed in Table 4, only the carbonate rocks with 2 to 20 parts per million of vanadium (4-35 ppm V_2O_5) have a lower average. Yet extremely important deposits of vanadium occur in sandstone deposits of Colorado, Utah, Arizona, New Mexico, South Dakota, and Wyoming. These deposits are in sandstones found on the Colorado Plateau and in sandstone beds flanking the Black Hills.

At Kara-Tau in Turkestan, U. S. S. R., extensive metamorphosed sandstone beds are reported to contain thin bands of roscoelite alternating with bands of flint.

Sandstone Deposits of the Colorado Plateau

Vanadium minerals have been recognized in many of the sandstone beds of the Colorado Plateau, and since the discovery of vanadium and uranium in the sandstones of western Colorado in 1898, more particularly since about 1950, considerable work has been done on the geochemistry and occurrence of vanadium and uranium.

Much of the literature relating to vanadium deposits on the Colorado Plateau refers to two general types of ore—the "roscoelite" type of Rifle and Placerville and the "carnotite" type of the Uravan Mineral Belt and elsewhere. "Roscoelite" is a distinctive and descriptive term that still can be used, although the important ore minerals include in addition to roscoelite, vanadium-bearing hydromica and small amounts of vanadium-bearing chlorite and montroseite. In the near-surface deposits of the Uravan Mineral Belt, carnotite was the principal ore mineral, hence the term "carnotite ores." With deeper mining in water-saturated rocks, the yellow carnotite ores have given way to black, unoxidized, low-valent vanadium and uranium oxides and silicates.

In general, the "roscoelite" type of vanadium ores occurs in relatively clean sandstone beds of the Entrada and underlying Navajo(?) formations: the "carnotite" type ores are found in the Morrison formation associated with carbonaceous material.

The vanadium-bearing ores of the Colorado Plateau also have been classified on the bases of vanadium-uranium ratio and amount or sequence of oxidation. The following discussion of mineralogy of vanadium-bearing ores, taken from Weeks, Coleman, and Thompson,[34] details the rationale for these classifications:

"Vanadiferous Ores"

"The primary vanadium-uranium ores are characterized in general by their black color and by the presence of low-valent uranium and vanadium oxides and silicates, and by copper, iron, lead, and zinc sulfides, arsenides. and selenides. These ores should not be confused with the blue-black or corvusite ores which represent an intermediate stage of oxidation. The ores have a wide range of vanadium content and for convenience in description they have been divided into groups on the basis of their vanadium-uranium ratios.

"Vanadium-Uranium Ratio Greater Than 15:1

"Vanadiferous ores with low uranium content are characterized by the dominance of vanadium silicates over vanadium oxides and by the general lack of fossil wood. The unoxidized ores in the Entrada sandstone (Jurassic) of the Rifle and Placerville districts in western Colorado are representative of this group and appear to have a monotonous and simple mineralogic composition. At Placerville roscoelite is the dominant vanadium mineral occupying the intergranular areas as fine-grained micaceous aggregates, and at Rifle it is accompanied by some vanadium-bearing chlorite and mixed layer mica-montmorillonite (or so-called hydrous mica). No vanadium hydrous mica is present in the primary roscoelite ore at Placerville. The chemical analyses of Placerville samples indicate that vanadium substitutes for aluminum; the high potassium and low water content are characteristic of roscoelite and not of vanadium hydromica. In roscoelite-rich thin layers either concordant with or cutting across bedding planes the quartz is strongly corroded and microstylolites develop where the quartz grains are in juxtaposition. Montroseite is interleaved with the roscoelite aggregates as small discrete crystalline rosettes. Paramontroseite may locally supersede montroseite where oxidation has commenced. Calcite or dolomite commonly accompanies the montroseite and roscoelite and appears to be contemporaneous with the vanadium mineralization. Minor but persistent galena-clausthalite (selenium and sulphur in solid solution) and chalcopyrite are accompanied by sparse pyrite and marcasite. Small amounts of uranium are present, but its mineralogic occurrence has not been determined completely. . . .

"Vanadium-Uranium Ratio Between 15:1 and 1:1

"Ores with vanadium-uranium ratios ranging between 15:1 and 1:1 occur extensively in the Salt Wash sandstone member of the Morrison formation (Late Jurassic) and to a lesser extent in the Shinarump member and other basal sandstones of the Chinle formation (Triassic) and in other formations.

"The uranium occurs in uraninite and coffinite in the primary ore and almost without exception is associated with coalified wood or other carbonaceous material and with pyrite or other sulfides. . . .

"Uraninite preferentially replaces the cell walls of the wood structure. . . . Where the original wood structure was collapsed or vitrainized or both during diagenesis, the uraninite intimately impregnates or replaces the coal and faithfully retains the coaly structures. . . . Coffinite is found within coalified wood where it fills the cell cavities. Most of the occurrences of coffinite are in vanadiferous ores, and many of these are in the Salt Wash sandstone member of the Morrison formation in the Uravan mineral belt of western Colorado." . . .

"In the primary ores of this group vanadium oxides appear to be more abundant locally than vanadium silicates. The chief primary oxide, montroseite VO(OH), is easily oxidized to the more commonly observed paramontroseite. Another primary vanadium oxide haggite V202(OH)3 has been identified from near Carlile, Wyo. and from several mines in McKinley and Valencia Counties, N. Mex. In places montroseite impregnates the fossil wood by filling cell cavities, but the growth of its elongate crystals soon obscures the wood structure. Typically its strong crystallinity causes the formation of rosettes and bands of intricate and sinuous nature either on contraction fractures in fossil wood or in interstitial areas of the sandstone.

"Associated with the montroseite and paramontroseite in the intergranular matrix are vanadium silicate minerals. Vanadium-bearing chlorite may be one of the most important vanadium silicates in the primary ores. Intensive study of a small number of samples by Hathaway indicates that roscoelite is not an important mineral in this group, but that vanadium hydromica, characterized as a mixed layer mica-montmorillonite clay, is commonly present and may contain considerable amounts of vanadium. The vanadium silicates impart a deep greenish or brownish color to the rock and in thin section show a moderate birefringence and a marked pleochroism. Kaolinite is common in the ores of the Grants district in New Mexico but only a small amount is present locally in the Uravan district of Colorado. Kaolinite does not contain substituted vanadium."

"Nonvanadiferous Ores

"Deposits in which vanadium is negligible and uranium is the only metal of importance—except where copper may be locally of commercial value—occur chiefly in the Shinarump member and other basal sandstones in the Chinle formation (Triassic). The ore is found mainly in channels that contain carbonaceous material and mudstone beds; these channels are along the thin edge (pinch-out) of the formation where conglomerate and sandstone beds fill cuts in the underlying formation. . . .

"In general these primary ores are lighter in color than the vanadiferous ores because the black vanadium oxide, montroseite, is lacking, but a few ores with high sulfide content are dark colored. Uranium is contained chiefly in uraninite, and coffinite is scarce or lacking. Coalified wood and diagenetic sulfides are the main controls of uraninite deposition. and the wood is replaced in the same manner as described above."

"Early Stage of Oxidation

"The primary ores are stable in reducing environments after emplacement and generally retain their original minerals and textures if the) are not exposed to oxidizing conditions. Those ores which have remained below the zone of oxidation (water table) retain their primary character. In the Colorado Plateau various stages of oxidation may be found superimposed on the primary ores because the deposits occur in many different situations with respect to the water table and also because of variable water-retention capacities of the pore space of the ore sandstones.

The numerous nonsilicate vanadium minerals are very sensitive to changes in oxidation potential and pH. Most of them have small fields of stability and therefore serve as convenient indicators of the degree of oxidation and the pH of the environment during oxidation. Montroseite. $VO(OH)$, oxidizes readily to paramontroseite, VO_2, when exposed to air, as evidenced by the fact that montroseite specimens in the laboratory commonly alter to VO_2 in a few months' time. Other new vanadium (IV) minerals—doloresite, duttonite, and simplotite—are possibly all alteration products of montroseite. ..."

"Corvusite Ore, Partly Oxidized

"Further oxidation of the ores causes a change in color from black to blue black in ores of the corvusite stage. Some greenish-black and brown also appear at this stage. As soon as all the vanadium (III) has oxidized to vanadium (TV), the vanadium (IV) minerals alter to a group of compounds containing various proportions of vanadium (IV) and (VI with some calcium, iron, sodium, or potassium.

"Available vanadium (V) combines with uranium (VI) to form the widespread but ill-defined and sometimes inconspicuous mineral rauvite which may be dispersed in microscopic grains in massive corvusite or form glassy or gel-like coatings on quartz grains, pebbles, or contraction fractures in mineralized wood. Rauvite ranges in color from purplish black and brownish red in the gel-like varieties to orange red in the powdery aggregates. Its chemical formula is uncertain because samples giving the same X-ray powder pattern have slightly different chemical compositions. The calcium content may not be essential but all rauvite samples have a higher V:U ratio than carnotite and tyuyamunite. The rare and even less well known mineral uvanite is intermediate in V:U ratio between rauvite and carnotite and was found with rauvite at Temple Mountain, Utah.

"Small amounts of several uranyl minerals including meta-autunite. phosphuranglite, saleeite, novacekite, uranophane, and boltwoodite, have been found in corvusite ore. These minerals form locally where uranyl ions are present and where the vanadium has not reached the quinquevalent state or where the pH is too low for formation of carnotite."

"Carnotite Ore, Highly Oxidized

"As oxidation progresses, carnotite and tyuyamunite develop chiefly from rauvite. and some may form in other ways (investigation in progress) . Once crystallized, the carnotite is remarkably stable and fixes the uranium very effectively. The minerals containing vanadium (IV) and (V) of the corvusite stage oxidize to form vanadium (V) minerals, lhe specific ones formed depend closely on pH conditions, on the presence of certain cations to combine with vanadium, and on several other factors. Vanadium fixes all available uranium in uranyl vanadates, and the excess vanadium may form the hydrated pentoxide, navajoite, or much more commonly it combines with other elements—these include calcium to form hewettite and pascoite and rossite, potassium and magnesium to form hummerite, sodium for sodium vanadate, aluminum for steigerite, iron for fervanite, copper for volborthite and tangeite (formerly known as calciovolborthite), or barium and copper for vesignieite. These vanadates range in color from brown through red, orange, yellow, and green to nearly colorless. Hewettite readily dehydrates to metahewettite and rossite dehydrates to metarossite. Other new vanadates include santafeite, a manganese vanadate, and a strontium calcium vanadate.

"Although the presence of tyuyamunite in the 'carnotite ores' of the Colorado Plateau has been known for many years, the relative abundance of the two minerals is not known quantitatively. Neither is it known how much tyuyamunite has been converted to carnotite (or vice versa) by cation exchange. . . .

"In the oxidized ores of the Uravan belt carnotite, tyuyamunite, and the various brightly colored vanadates are locally abundant but in the bulk of the ore are actually less abundant than the fine-grained greenish-gray and light-brown vanadium silicates that contributed much of the vanadium mined in the Plateau previous to World War II. . . . The outcrop of ore sandstone is commonly gray with little or none of the brightly colored minerals. . . . These gray sandstone ores have commonly been termed roscoelite ores in contrast to carnotite ores, but preliminary study suggests that true roscoelite is common only in the Rifle and Placerville districts of Colorado. In the Uravan belt vanadium-bearing chlorite, and hydrous mica or mixed-layer clays seem to be more abundant than true roscoelite. Some of the vanadium silicate interstitial in the sandstone probably has persisted practically unchanged from the unoxidized ore, whereas some clay may have become impregnated with vanadium solutions migrating during oxidation.

"At the Rifle mine near Rifle, Colo., where the vanadium silicate ore is affected very little by oxidation, small amounts of the uranyl carbonates bayleyite and swartzite form efflorescences on the mine walls. Here probably little or no soluble vanadium is available to combine with the uranium."

As can be inferred from the above discussions, the range and degree of oxidation is of importance second only lo the range of primary composition. Oxidation, which depends upon access of air to the ore. is accelerated in rocks with little or no soil cover and relatively continuous permeable sandstone beds above the water table and in strata truncated downdip by a canyon. Where water is held in the pore space of the ore-bearing sandstone, oxidation has been prevented or retarded.

Evans '•' reviews crystal structure investigations on vanadium oxides. and the structure studies are compared with an oxidation potential—pH phase diagram which was constructed from thermodynamic data for vanadium. Evans summarizes:

> "Referring once more to Figure [2], it is useful to indicate on the Eh-pH diagram the regions in which the various minerals which have been discussed are stable. This has been done in Figure [3], in which the direction of alteration is also suggested by means of arrows. The focal point is montroseite, the most reduced state of vanadium oxide minerals. The alteration under weathering then moves upward on the diagram, with excursions to higher or lower pH conditions, depending upon mineral associations and environment. In the region of complete oxidation. the presence of uranium causes the various complex fields above the shaded boundary to be completely replaced by carnotite.
>
> "Broadly speaking, the following generalizations may be made in conclusion:
>
> 1. Trivalent vanadium is represented by the primary mineral montroseite (VO(OH)), and is readily oxidized by the atmosphere to the quadrivalent form. Vanadium is similar in its crystal chemistry to manganese in the three- and four-valent state.
>
> 2. Mixed vanadium(IV) and (V) oxides comprise the 'blue-black ores,' and probably are derived to a considerable extent from oxidation of montroseite.
>
> 3. Vanadium(V) oxide and its derivatives form the final stage of oxidation. In alkaline media, vanadates behave structurally like phosphates; in acid media, vanadates condense successively to form colorless and orange-red soluble complexes, and finally slightly soluble red or brown fibrous hewettite-type compounds. Vanadium(V) is similar to molybdenum and tungsten in behavior with regard to the tendency to polymerize with decreasing pH.

An important structural property of pentavalent vanadium is the formation of the five-coordinated chain which appears between pH 2 and 8. This structure motif appears to play an important role in the formation of the mixed vanadium(IV) and vanadium(V) oxides and hydrates.

Carnotite covers a wide pH range of stability for vanadium(V). Pentavalent vanadium will precipitate any uranium present as carnotite or tyuyamunite. Excess vanadium may be temporarily deposited as hewettite or pascoite, or bound up in a silicate mica or clay.''

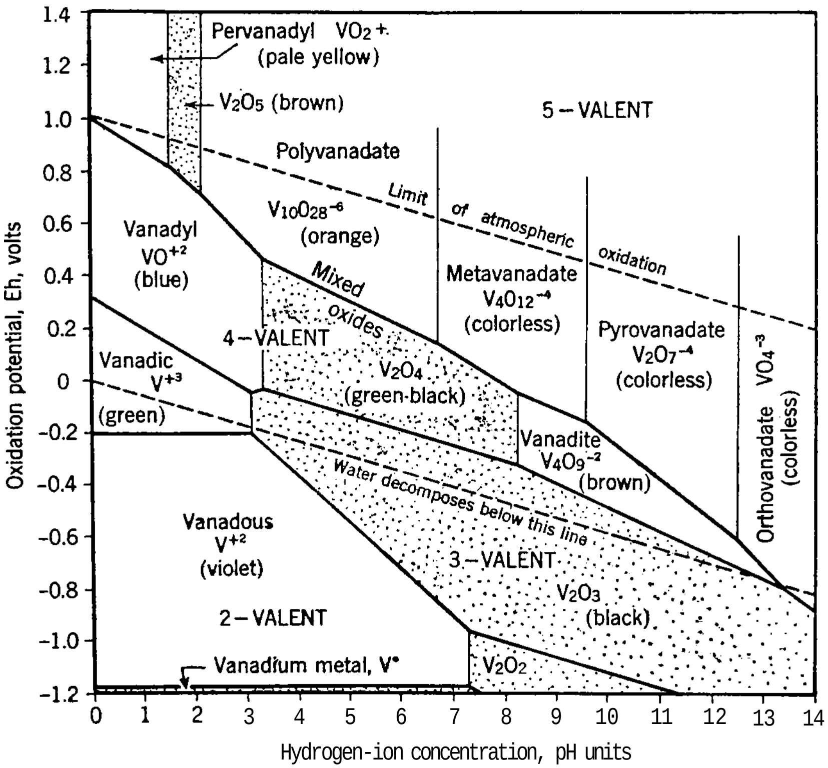

Figure 2.—Oxidation potential—pH phase diagram for vanadium in aqueous solutions. Stippled fields represent solids (solubility of $V<0.01$ mol. per 1.). Phases may be hydrated or hydrogenated to an unknown degree. (U. S. Geol. Survey Prof. Paper 320, p. 92.1

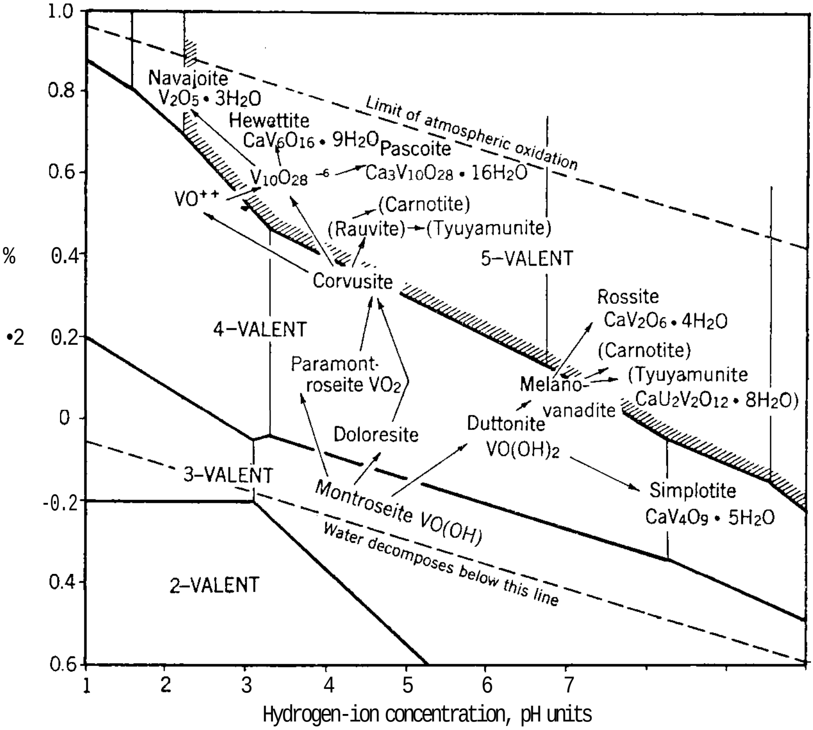

Figure 3.—Portion of the Eh-pH phase diagram of Figure 2, showing positions of various vanadium mineral species and probable alteration sequences. (LI. S. Geol. Survey Prof. Paper 320, p. 101.)

In southwest Colorado and adjoining parts of Utah, Arizona, and New Mexico, sedimentary rocks are exposed ranging in age from the Pennsjlvanian Hermosa formation to the Eocene Wasatch formation.

Although uranium and vanadium deposits have been recognized in most of the sedimentary formations, the major production has come from rocks of Triassic age (Shinarump formation and Chinle formation) and from Jurassic rocks (Entrada sandstone and Morrison formation). A general stratigraphic section is given in Table 6.50

In the descriptive material accompanying Mineral Investigations Field Studies Map MF 16, Finch "7 discusses the general geology of the Colorado Plateau:

"The Colorado Plateau consists of highly dissected mesas with altitudes ranging from 4,500 feet to 7,000 feet. Small laccolithic mountain ranges rise above the general level of the mesas. Sedimentary rocks ranging from Paleozoic to Tertiary age crop out on the Colorado Plateau. Igneous rocks consist mainly of groups of laccoliths and stocks and scattered plugs, dikes, and flows. Anticlinal and monoclinal structures are common throughout the Colorado Plateau. In western Colorado and eastern Utah, however, the major structural features are parallel northwest-trending anticlines, which are the result of upwelling of salt and gypsum. The outcrop pattern of the major uranium-bearing beds generally reflects the structures.

"Uranium occurs in many formations on the Colorado Plateau, but most of the deposits are restricted to a few formations. . . .

"The Shinarump conglomerate of Late Triassic age, which ranges in thickness from a knife-edge to 225 feet, consists mainly of light-colored strata of conglomerate, sandstone, siltstone, and mudstone. The Shinarump unconformable overlies the Moenkopi formation of Early and Middle Triassic age. The unconformity is erosional, and locally sedimentary rocks of the Shinarump fill channels cut into the Moenkopi. The channels make up about 5 percent of the area of the Shinarump conglomerate. The uranium deposits are found mainly in channels that contain carbonaceous material and mudstone beds. The Shinarump is present only in Arizona, New Mexico, and part of southern Utah. Most of the large uranium deposits of the Shinarump are found in channels near irregular pinch outs of the formation.

"The Chinle formation of Late Triassic age ranges in thickness from a knife-edge to 1,000 feet and consists of a thick series of mudstone, sandstone, conglomerate, and limestone beds. In some places in Utah a prominent sandstone named the Moss Back member by Williams and Stewart . . . forms a part of the lower Chinle. Where the Moss Back forms the base of the Chinle it overlies the Moenkopi or older formations with an erosional unconformity. In these places the Moss Back is a major uranium-bearing zone. The Moss Back member is similar to the Shinarump conglomerate in lithology and stratigraphic position and was cor-

related with the Shinarump by early workers. This member pinches out in many places in eastern Utah, and channels near the pinchouts seem the most favorable sites for large deposits. In some places in Utah and Arizona uranium deposits are found in siltstone beds in the lower part of the Chinle.

"The Entrada sandstone of Late Jurassic age consists of light-orange crossbedded sandstone that forms a characteristic smooth cliff, called the slick rim; it averages about 50 feet in thickness in western Colorado. The Entrada is a clean, partly aeolian sandstone that rarely contains mudstone and carbonaceous material. In parts of western Colorado the Entrada contains principally vanadium deposits . . .

"The Morrison formation of Late Jurassic age ranges in thickness from 500 to 900 feet and in general can be divided into an upper mudstone member (Brushy Basin) and a lower interbedded sandstone and mudstone member (Salt Wash). Most of the uranium deposits are found in the upper sandstone beds of this lower, interbedded, sandstone and mudstone member. These beds are light-brown, medium-grained, and locally contain abundant carbonaceous material and light-colored mudstone beds. The sandstone is generally lenticular and is of fluvial origin. The largest deposits in the Morrison formation are in western Colorado and northwestern New Mexico."

Significantly, vanadium and uranium in the ores varies in relative abundance both geographically and stratigraphically. In general, deposits of vanadium with little uranium are found in the Entrada and Navajo(?) sandstones on the extreme eastern margin of the Plateau. The Morrison formation, particularly the Salt Wash member in the Uravan Mineral Belt of western Colorado contains deposits with the vanadium-uranium ratio commonly between 4:1 and 10:1. The vanadium-uranium ratio in the Morrison formation is slightly lower in the Green River and the Henry Mountains districts of Utah, and is much lower toward the south in New Mexico. The deposits in the Shinarump conglomerate and in the basal sandstones of the Chinle formation have a much wider range of composition than those in the Entrada and Morrison formations. Vanadiferous uranium deposits with the vanadium-uranium ratio between 5:1 and 1:1 occur at Monument Valley, Arizona; Big Indian Valley, San Juan County, and Temple Mountain, Emery County, Utah.

The principal vanadium-uranium regions in Colorado, comprising only a portion of the Colorado Plateau proper, are shown in Figure 4. Because of scale limitations Figure 4 does not show the location of individual mines or generalized surface geology. Information relating to distribution of deposits and surface and subsurface geology is given on excellent maps by Finch 57 and Hague, Goldenstein, and Blakey.58

The Colorado Plateau vanadium and uranium deposits are described in many published papers; some of the more important references with additional bibliographies accompany this report.51* 00 01 u- c1 ui '" 0i 07 G8 09

Uravan Mineral Belt, Colorado: In the Uravan Mineral Belt (Uravan and Gateway districts, Colorado, Figure 4) the large mines are in the upper sandstone lens of the Salt Wash member of the Morrison formation. Lesser production has been developed in the lower part of the Salt Wash member or in the base of the overlying Brushy Basin member of the Morrison formation.

The most common type of host rock is the lenticular sandstone facies of fluviatile sediments. Because carbonaceous material is found associated with many ore bodies, in exploration the presence of this carbonaceous material is recognized as an important favorable criterion. Altered volcanic debris is abundant in certain zones of the Brushy Basin shale member above the Salt Wash sandstone member of the Morrison formation. Lesser amounts are present within the ore-bearing sandstones.

The deposits are tabular, elongate, or podlike, in general parallel to the bedding but commonly with a gently undulant surface. Locally the ore boundary crosses the bedding in steep curved surfaces referred to as "rolls." Individual deposits tend to be grouped in clusters and range in length from a few feet to a thousand or more feet; in thickness from a few inches up to 10 to 15 feet, but rarely more than 30 feet; and contain from a few tens of tons to thousands of tons of ore. The ore may follow the bottom of the channel or sandstone lens or the top of a lens or sedimentary structure. A single deposit may range in grade from weakly mineralized rock to strongly mineralized massive or disseminated ore. Ore boundaries range from a sharp distinct cutoff within a fraction of an inch to a broad transition zone. Guides to ore in the Uravan Mineral Belt are described by Fischer, Weir, Hausen, McKay, and Hastings.

Fischer15- states:

> "The Morrison sandstone beds containing the ore deposits are lenticular and in places 50 feet or more thick. They are interbedded with mudstone. The sands were deposited in channels and on flood plains of streams that meandered widely across the surface of low relief and grade. Most of the carnotite deposits seem to occur in or near the thicker central parts of the lenses; the portions of the channel sands that occupy meander bends seem to be particularly favorable for ore deposits in some areas. In places the channel sands form well defined lenses, some only a few hundred feet across and these can be recognized at the outcrop or in cross sections through drill holes.

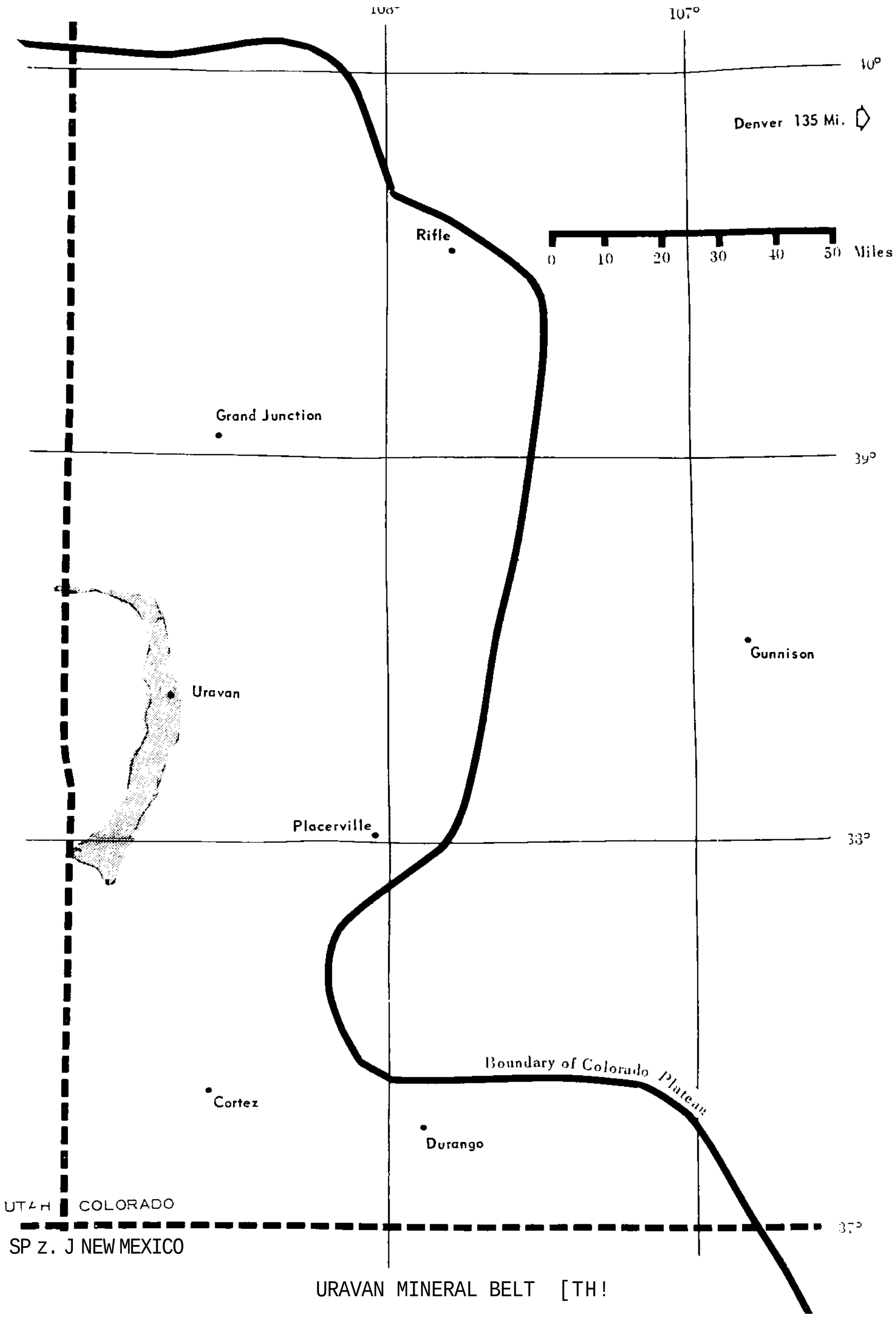

Figure 4.—Sketch map showing location of Uravan Mineral Belt and approximate outline of Colorado Plateau in Colorado.

> Other sandstone lenses are broad and vaguely defined. The trend of the channel sands commonly can be determined by observations of bedding and locally by the orientation of fossil logs . . . The sandstone in the central parts of the channels is dominantly medium grained, medium- to thick-bedded or irregularly bedded and moderately clean, although some mudstone in the form of grains, pebbles, and small lenses is common. Lenses of sandstone, less than about 20 feet thick which might have been deposited in small or short-lived channels or on flood plains bordering the main channels, rarely contain sizeable ore deposits. Such sandstone is dominantly fine grained, thin bedded, and either clean or argillaceous."

After studying the geologic logs of about 2500 holes drilled in the Morrison formation of southwestern Colorado, Weir™ concluded:

> "(1) Most ore deposits are in or near the thicker central parts of sandstone lenses and in general the thickness of the sandstone decreases away from the deposits. Sandstone that is less than 40 feet thick is generally not favorable for large ore deposits.
>
> (2) Sandstone in the vicinity of ore deposits is colored light brown, but an increasing proportion of sandstone away from ore deposits has a reddish color which is indicative of unfavorable ground.
>
> (3) Near ore deposits the mudstone in the mud-bearing sandstone and immediately below it has been altered from red to gray. The amount of altered mudstone decreases outward from ore deposits, for sandstone in the immediate vicinity of ore deposits contains more carbonized plant fossils than do the same beds away from ore deposits, suggesting that ore deposits are localized in the vicinity of abundant carbonaceous material."

The favorable relationship of zones of bleached sandstone in the Uravan Mineral Belt to concentrations of uranium and vanadium mineralization has been noted by Hausen.[71] He recognizes that an increase in stage of alteration accompanies increase in mineralization, argillization, asphaltization, corrosion of sand grains, and ratio of matrix minerals to sand grains. By use of textural and mineralogical features, Hausen classifies alteration into five different stages of replacement:

> "The initial stage is usually found in barren sandstone and may be referred to as the orthoquartzite stage or the most advanced stage of diagenetic alteration prior to epigenetic replacement. Sand grains have been silicified into interlocking. sutured anhedra. Authigenic quartz fills nearly all interstices.

> More than ninety percent of the rock is composed of quartz. feldspar and chert.
>
> "Incipient stages of replacement occur along peripheral zones of ore bodies. Replacements are initiated along zones of access or weakness between phase boundaries. Overgrowth boundaries and strained contacts become edged with vanadiferous illite. Seventy to ninety percent of the rock is made up of quartz, feldspar and chert.
>
> "Intermediate replacement stages generally occur inside zones of ore proper. Replacements are sufficiently progressed along boundaries of weakness to completely isolate secondary growths from primary grains. Authigenic quartz is apparently more soluble than allogenic quartz, and is largely replaced before appreciable etching of detrital cores occurs. Sixty to seventy percent of the rock is composed of quartz, feldspar and chert.
>
> "Advanced stages of replacement occur within major ore zones. Diagenetic overgrowths have been almost entirely replaced by epigenetic assemblages. Allogenic grains of quartz are highly corroded and display scalloped replacement edges. Forty to sixty percent of the rock is composed of quartz, feldspar and chert.
>
> "The final stage of replacement is seldom reached in Salt Wash ore bodies. It is approached only along high grade ore seams where host minerals are virtually effaced by replacements of clay and ore minerals. Only sparse spicule-shaped quartz relics remain."

McKay7J shows that coincidence of lenticularity, favorable color of sandstone, and continuous gray mudstone underlying the sandstone are necessary for large deposits. Lenticularity without other characteristics is unfavorable in the Gateway-Uravan district in Colorado. At the surface the favorable sandstone is buff with scattered brown speckles; at depth it is white or light gray with disseminated pyrite grains, in contrast to the average red sandstone of the Salt Wash member of the Morrison.

Hastings 73 has examined many deposits in the Uravan Mineral Belt and as a result of these studies he states:

> "The most significant tonnages are usually located in what are termed 'channels' or elongate sandstone lenses, generally measuring at least one-half mile in width and two miles or more in length. The ore-bearing sandstone in these channels is consistently thicker than in areas outside the channels. The host rock in the vicinity of ore bodies exhibits certain favorable criteria, the most important of which are:

1. Good sandstone thickness, 35-90 feet
2. Alteration of the primary red coloration of the sandstone to various shades of gray or light brown
3. Alteration of basal and interbedded mudslones from primary red to gray or greenish colors
4. Presence of carbon
5. Certain fluvial features such as cross-bedding and festooning."

Further description of the stratigraphy of the Morrison formation and guides to uranium-vanadium deposits in western Colorado are given by Craig and others.74

Since 1900, vanadium production from the Uravan Mineral Belt has amounted to approximately 69,000 short tons of contained V^O.-,.

Exploration and Development:

Better geologic understanding of the distribution of ore and ore controls in the Uravan Mineral Belt has reduced exploration risks and permitted successful exploration along trends into deeper ground. Exploration in most untested areas is by diamond core drill. Because many of the shallow deposits already have been found, much of the current exploration is for deeper-lying channels. Holes are collared on the upper surface of Dakota formation, and drilling depths range from 600 to 800 feet.

Hastings 73 has outlined a sequence of steps generally followed in a diamond-drill exploration project:

"1. When possible, a field study of outcrops and any existing mines is made to determine the probable trend of the channel to be explored. If previous drilling information is available, it is carefully examined.

"2. Initial wide-spaced drilling. In this first stage of drilling an attempt is made to approximately delineate the channel boundaries as well as to roughly outline the more favorable areas within the channel. The holes in this first stage of drilling are spaced 1000 feet apart, or greater, along lines transverse to the postulated long axis of the channel. These lines, or 'fences,' of holes are spaced in a parallel pattern 1000 to 2000 feet apart, where topography permits.

"3. Upon completion of this first stage of drilling, closer spaced holes are drilled, 400 to 600 feet apart, offsetting the more favorable holes. At this point in the exploration project it is hoped to find ore or strong mineralization.

"4. Any ore or significantly mineralized hole found in the second stage of drilling is then blocked out on 200 foot centers. In blocking out reserves on this spacing, either

> the rectangular method or the 60 degree equilateral triangle method is used, with the legs of the triangle measuring 200 feet. For those who are familiar with the erratic nature of Salt Wash ore bodies, and who might think 200 foot spacing is excessive, it should be pointed out that economics dictate that at these drilling depths it is not feasible to move closer. Also, past experience has shown that this spacing, when coupled with long hole drilling underground, provides sufficient geological information and reserve data to plan mining operations."

In addition to diamond-drill coring, rotary plug drilling to depths of less than about 300 feet and wagon drilling to depths of about 180 feet are used in conjunction with coring for blocking out reserves and for limited prospecting. These costs are appreciably cheaper than those for diamond-core drilling.

Underground long-hole drilling is used in the deeper mines to prospect between surface drill holes and to provide additional control for mining.

Calculation of ore reserves requires a consideration of geologic conditions; Hastings 73 describes a standard method:

> "The polygonal method is used to determine reserves developed on 40 to 60 foot centers. The area of influence of each ore hole is extended one-fourth to three-fourths the distance to an offsetting mineralized hole, depending on the degree and thickness of mineralization in the offset hole. It is assumed that ore is continuous between ore holes drilled on 50 foot centers, providing the ore occurs at approximately the same position in the ore-bearing sandstone.
>
> "Calculations of reserves from holes drilled on 200 foot centers are based on empirical formulas derived from studies of areas that have been extensively mined and drilled. It is found that in a large favorable area, 1000 by 1000 feet, or larger, that has been uniformly drilled on 200 foot centers, the area underlain by ore approximates 60% of the ratio of ore holes to total holes drilled. Total reserves, positive and indicated, are calculated as follows:

t * 1 _ (A) (T) Ho
Total reserves ——————— X — = — X 0.60
14.5 Ht
A = total area
— = ratio ore holes to total holes
Ht
T = average thickness of ore
14.5 = tonnage factor for average Salt Wash ore

"Positive reserves are calculated for each ore hole as 500 tons per foot of ore grade material penetrated. The sum of the positive reserves for the area under study is subtracted from the total reserve figure, and the remainder classified as indicated reserves. At 700 foot depths to the ore zone, a minimum of 40,000 tons of positive ore of average grade is needed to justify shaft entry."

Mining Costs:

High underground mining costs in the Uravan district are an important consideration in estimating reserves and resources; $20.00 a ton as compared to $11.00 to $15.00 elsewhere on the Colorado Plateau and to S5.00 to $8.00 a ton for open-pit operations. Several factors contribute to the high cost. Many of the Uravan deposits are thin, averaging no more than 3 feet in thickness, and are undulating and discontinuous. A slow mining rate usually is necessary to prevent excessive dilution. Another important factor in mining costs is the selection of the mining method and equipment that will give the most economical extraction with the highest profit.

Peck[73] has estimated total mining costs for the Uravan Mineral Belt to be:

	Cost per Ton	
	Range	Average
Exploration	$ 1.25 - $ 6.40	$ 2.00
Depreciation of plant and equipment	1.25 - 2.85	2.00
Development	2.90 - 4.40	3.00
Direct mining	7.85 - 27.00	10.10
Indirect mining	1.05 - 4.90	2.20
Total	$14.50 - $34.00	$19.30

The high charge per ton for exploration in the Uravan Mineral Belt is a reflection of the erratic nature of the deposits and the increasing depth at which deposits are found. Interpretation between drill holes is required to calculate the size and grade of an ore deposit from drill data. In the Uravan Mineral Belt even close-spaced drilling is not too reliable. Application of long-hole drilling has lowered costs for underground exploration. Underground exploration is necessary, and because of the large amount of drifting in waste between ore lenses, development costs are high.

For items that can be identified, Peck has estimated the direct mining costs in the Uravan Mineral Belt to be:

Cost per Ton	
Labor	$6.50
Powder	1.20
Bits and rods	0.40
Maintenance	1.40

Increased production rates and reduction in labor costs through use of suitable large-scale mechanized equipment is a common approach to lower mining costs. A controlled mining rate minimizing dilution offers an opportunity for a reduction in cost per ton by means of increased grade.

An important part of indirect costs goes for taxes and insurance. Including Federal and State unemployment compensation, severance tax, property tax, and old-age and survivor's benefits, taxes and insurance will amount to at least $0.60 a ton.

Rifle Creek-Placerville Districts, Colorado: Ores of the roscoelite, hydromica, chlorite, and montroseite type are found principally in a belt extending from Rifle, in Garfield County, Colorado; through Placerville, in San Miguel County, Colorado; and Rico, in Dolores County, Colorado, to Lightner Creek, near Durango, in La Plata County, Colorado. The ores in the Entrada and Navajo (?) formations have been worked mainly for vanadium. The uranium content has only minor byproduct value. The average thickness of ore layers and the number and size of ore bodies decrease southward. The total amount of ore in the layer at Placerville probably is several times that at Rico, and many times that at Lightner Creek. Commercial production has been limited almost entirely to the Rifle and Placerville occurrences.76

Rifle Creek Vanadium Deposits:7778 In the Rifle Creek area the Rifle-Garfield deposit, one of the larger deposits of the Plateau region, is partly in the Entrada sandstone but mainly in the underlying Navajo (?) sandstone. Most of the characteristics of the deposits of the Colorado Plateau are also found in the Rifle Creek area along with other unique features. Both sandstones, the Entrada and Navajo (?), are composed entirely of clean, fine-grained sandstone and lack the abundant shaly and carbonaceous materials occurring in the sandstone hosts of most of the ore-bearing formations of the Colorado Plateau region.

The Rifle-Garfield deposit is large; it is at least 10,000 feet long and may have contained as much as 25,000 tons of V205 before mining and erosion removed part of the ore. Consisting of fine-grained minerals that impregnate the sandstone host, the ore contains from 1 to 3 percent V^O.-, and several hundredths percent U308. The ore minerals color the rock gray, and the color darkens as the vanadium content increases. The ore occurs in three, partly overlapping, tabular layers that lie nearly parallel to the formation contacts, but are not concordant with the bedding in detail. Each vanadium layer is bordered on one side by a thin layer. generally about %-inch thick, of finely disseminated material containing lead and selenium. This lead-selenium layer, in turn, is bordered by a one- to two-foot-thick layer of greenish sandstone containing a finely micaceous chromium-bearing mineral. The lead-containing band ma) be difficult to recognize and is locally absent.

The accompanying lead, selenium, and chromium bands are concentrated in thin layers adjacent to the vanadium-uranium ore. Lead and selenium below the zone of complete oxidation are combined in minute grains as a solid-solution mixture of galena (PbS) and clausthalite (PbSe I. On oxidation, the galena-clausthalite grains alter to cerussite (PbCOs), some of which has a reddish internal reflection that might be caused by native selenium. The chromium-bearing layer is light green to grayish green and contains a green, micaceous, fine-grained material that fills the sandstone pores. This chromium-bearing sandstone closely resembles the chromium-bearing layer associated with the vanadium-uranium deposits at Placerville, Colorado; Hess711 suggested that the chromium-bearing mineral at Placerville is mariposite.

The principal ore minerals are vanadium-bearing silicates of micaceous habit. They have been identified as the vanadium mica roscoelite and as unnamed varieties of a mixed layer mica-montmorillonite (hydromica) and small amounts of vanadium-bearing chlorite and montroseite. Associated with these two vanadium-bearing silicates is the same general suite of minerals and accessory elements found in many of the sandstone deposits in which vanadium and uranium occur together.

The Rifle Creek deposit is unique in the high vanadium-uranium ratio, the lack of carbonaceous material, and the abundance of roscoelite. In other respects the deposit is similar to vanadium-uranium deposits of the Colorado Plateau.

In the vicinity of the Rifle Creek vanadium deposit the top few feet of the underlying Chinle formation is altered from red to gray. This altered zone extends about 2,000 feet north of the deposit and a few hundred feet south of it. Fischer suggests that the presence of this altered zone at the top of the Chinle formation and its apparent association with the vanadium deposit increased the size of the target to such an extent that a pattern of drill holes spaced about a half mile apart would have found the deposit or the associated altered zone in the Chinle.

Although the area was discovered about 1909, there was little or no production before 1925. From 1925 to 1954 the total production of vanadium ore from the Rifle Creek area was about 750,000 tons, containing approximately 12,500 tons of V2O5.

Placerville Vanadium Deposits:10 s" sl In the Placerville area the ore is a sandstone impregnated with vanadium minerals. Most of the ore that was mined contained 1Vi> to 3 percent VL.0fl and was l1/^ to 15 feet thick. The ore was found in lens-shaped masses lying nearly parallel to the bedding but not conforming to it in detail. These masses are in the upper 25 feet of the Entrada sandstone and occur in two belts, through which the ore bodies appear to be widely scattered. In their report on the Placerville deposits Fischer, Haff, and Rominger *" suggest that one mineralized belt, extending from the Bear Creek mine northwestward to the Omega mine and northward along Leopard Creek, is at least 9 miles long and about l]/2 miles wide. What appears to be a second belt is exposed north and east of Sawpit. The northern limits of this second belt are not known, but it may extend northwestward to the vanadium-bearing outcrops on Leopard Creek. A useful horizon marker is a thin layer of light green sandstone, colored by a finely disseminated chromium mineral, probably mariposite, which lies a few feet below the vanadium-bearing layer in the Bear Creek mine-Leopard Creek belt.

The principal ore mineral is roscoelite which occurs in minute micaceous flakes coating sand grains and partly or completely filling the spaces between the sand grains. The ore ranges from dull greenish-gray to dark gray, and in general it becomes darker as the vanadium content increases. Small, irregularly shaped quartzitic nodules and lenses are commonly enclosed in the ore, especially in ore of relatively high grade.

The individual vanadium ore bodies have a wide range in size. The small ones are only a few feet across; the larger ones, up to several hundred feet across and from two to twenty feet thick, contain many thousand tons of ore. The known ore bodies of the larger mines appear to be distributed irregularly, but they are clustered in poorly defined areas 1,000 to 2,000 feet across. Additional deposits in the Placerville area may be difficult to find because of deep drilling depths over a large part of the area.

From 1910 to 1920, 194,496 tons of ore were milled and approximately 3,325 tons of V2O5 were recovered.

Colorado Plateau Deposits of Utah, Arizona, and New Mexico: The uranium and vanadium sandstone deposits of the Colorado Plateau extend into Utah, Arizona, and New Mexico. Similar in certain respects to the deposits in Colorado, the deposits in Utah, Arizona, and New Mexico differ in that the vanadium-uranium ratio is much lower than for deposits in Colorado. They also differ in that important deposits occur in the Shinarump conglomerate and basal sandstones of the Chinle formation as well as in the Morrison formation. Although no vanadium has been recovered from uranium ores in the Todilto limestone in the Grants-Laguna area of New Mexico, the ores have a vanadium-uranium ratio of about 1 to 2.

In the Shinarump conglomerate and the Chinle formation, uranium deposits low in vanadium are found mainly in channels cut into the underlying formations near irregular pinch outs of the formation. Carbonized wood fragments or logs, altered gray mudstone, and lenticular sandstone and mudstone in the channel filling indicate a favorable environment.

Sandstone Deposits of Wyoming and South Dakota

Uranium-vanadium deposits similar to those on the Colorado Plateau flank the Black Hills in South Dakota and Wyoming. These deposits have a relatively low vanadium-uranium ratio and on an average contain 0.25 percent VL.05. The uranium deposits in the Gas Hills area, Wyoming, contain only trace amounts of vanadium.

Residual Sediments

Mainly because weathering has removed the soluble vanadate ion, residual sediments generally are lower in vanadium than the average of the upper lithosphere. An important exception to this statement is the black sands derived from the erosion of titaniferous magnetite deposits. These black sands commonly contain from 0.1 to 0.3 per cent V20B and are an important potential source of iron and vanadium.

Vanadate Deposits

Vanadium cappings of oxidized massive sulfide bodies have in the past been important sources of vanadium. In South-West Africa this still is true. However, deposits of this type do not appear to be important potential resources. Typically, vanadate deposits are in carbonate country rock in areas of deep oxidation and moderately arid climate. Evidence differs as to the source of these deposits.7

Vanadate Deposits of Southwestern United States and Mexico

In Arizona, New Mexico, and the main Cordilleran region of Mexico from the state of Chihuahua south to Hidalgo, vanadates of lead, zinc, and copper have been produced from a number of base-metal deposits. In general, these deposits are in areas of deep oxidation in a moderately arid climate. The vanadate minerals, vanadinite, cupro-descloizite, descloizite. mottramite, and mimetite, are found irregularly distributed in the oxidized portions of the ore bodies.

Vanadate Deposits of South-West Africa

South-West Africa, an important source of vanadium, has produced about 15 percent of the world's total. Deposits are in the dolomites of the Otavi Mountains in the Grootfontein-Tsumeb area.18 82 s:! 84 85

The vanadium-bearing minerals, descloizite, cupro-descloizite, vanadinite, and mottramite are mined from pipe deposits or steeply dipping vein-shaped bodies in the oxidized zones in the Otavi Dolomite Series.

Vanadium minerals in many deposits are associated in the oxidized zone with lead, zinc, and copper minerals. Sulfides may or may not be present or be related to the vanadium deposits.

Vanadate Deposits of Northern Rhodesia

The deposits of Broken Hill, Northern Rhodesia, occurred in massive dolomites of the Katanga System.:!S și 87 88 With the exception of one deposit which was almost wholly oxidized, the ore bodies consisted of a core of massive zinc-lead-copper-iron sulfides, surrounded by an irregular zone of oxidized ore. Although vanadium tended to concentrate along the margins of ore bodies, vanadium minerals—vanadinite and descloizite—were widely although irregularly distributed throughout the oxidized zones. The oxidized ores ranged from 0.75 to 2.09 percent V20,-,.

RESERVES AND RESOURCES

Vanadium ranks eighth among the minerals in order of abundance in the earth's crust. It is more plentiful than many so-called common metals such as chromium, zinc, niobium (columbium), copper, molybdenum, tungsten, lead, and others; but commercial production of vanadium has been from only a relatively few deposits. Except for the Minas Ragra deposit of Peru most of the vanadium production has resulted as a co-product or byproduct of mining for uranium, iron, titanium, phosphorus. zinc, lead, molybdenum, and copper.

In considering reserves and resources of vanadium, care must be taken not to confuse and use synon\mously the terms "reserves" and "potential resources." The term "ore reserves" connotes tonnage that might be mined under current economic conditions. "Potential resources," conversely, suggests the amount of ore that might be discovered and eventually mined under suitable but possibly different economic and technical conditions and with the possible stimulus of price increase. Reserves often are developed by companies to cover a two- to five-year period, whereas resource studies may look forward 25 to 100 or more years.

The most comprehensive published statement of vanadium reserves and resources is given in Chapter VIII. Section A, Report of the Committee on Refractory Metals, Materials Advisory Board.40 In Chapter VIII-A the Vanadium Raw Materials Group estimated the potential production and resources of vanadium from domestic and foreign sources. In the following discussions of potential resources, considerable use has been made of estimated grade, reserve, and resource figures given in Chapter VIII-A. Figures released by the U. S. Atomic Energy Commission also have been used as well as reserve estimates published by other investigators. In the latter case, for many deposits, the comparative magnitude of vanadium resources has been indicated rather than given in terms of actual estimated tonnages. Reserve figures undoubtedly have been estimated by producing companies for their own holdings, but commonly this information is of proprietary interest and has not been disclosed.

The problem of obtaining meaningful resource or reserve estimates is summarized by the Panel on Vanadium:40

> "Although there is no doubt that the total resources of vanadium are very large, only a rough appraisal of these resources can be made. Precise reserve figures are not available from many productive or potentially productive deposits, either because of incomplete development or company policy. Furthermore, because much vanadium is obtained as a coproduct or byproduct of other commodities, appraisals of available reserves of vanadium are influenced by the reserves and mining economics of these commodities."

This present study follows the report of the Vanadium Panel and gives an estimated tonnage for those deposits or districts where sampling and development are adequate to express quantitative figures. Semi-quantitative estimates will be given for those vanadium sources where tonnage and grade information is incomplete or where it is reasonable to assume that exploration will result in the discovery of additional deposits.

In general, "very large" refers to deposits or districts with possible potential resources of 100,000 or more short tons of vanadium pentoxide; "large" would indicate from 10,000 to 100,000 short tons of V_2O_5; "moderate" would be from 1,000 to 10,000 short tons of V_2O_3; and the potential resources of a "small" deposit would be less than 1,000 short tons of vanadium pentoxide.

Estimated grade, reserve, and resource figures are summarized in Table 7.

North America

Major North American production of vanadium has been from the Colorado Plateau sandstone deposits of Colorado, Utah, and Arizona, and from similar deposits in South Dakota and Wyoming. Potentially important sources of vanadium also exist in the phosphate rocks, carbonaceous shales, and titaniferous magnetite deposits of Idaho, Utah, Nevada, Wyoming, and New York, as well as in the Quebec and Ontario Provinces of Canada.

TABLE 7
VANADIUM PENTOXIDE—GRADE, RESERVES, RESOURCES

(Adapted from Table 1, p. 231, Chapter VIII-A,
Mineral Advisory Board Report)

Locality and Type	Grade Approx. %	Cnown deposits Short tons V2O5	Resources (i) lemi-'iucintita-.' Known and undiscovei'L-c
United States:			
Colorado	1. ::	52,000	Verv la,-
Colorado Plateau: Uravan Mineral Belt	1. 25 - 1. 75	15,000	La: rge-very .:.•
Colorado Plateau: "roscoelite" deposits	0. 10 - 0.25	u'5,000	Very lai"t =
Utah, Arizona, New Mexico Colorado Plateau: low V-high U deposits	0.25	800	Mod t* rate
Wyoming, South Dakota BLack Hills: Low V-high U sandstone deposits	0. 7 - 1.0	550,000	Very Larii
	0. 11 - 0. 29		Very large
Idaho, Montana, Wyoming, Utah, Nevada, Colorado: vanadium-bearing organic shales	0. 6	7 2,000	Ver.- targe
	U. 25 - 0. 45	400,000	Very large
Idaho, Montana, Wyoming, Utah: vanadium-bearing phosphate deposits	0. 2 - 0. 5		Very larg..-
Wyoming			Small
Iron Mt.: titaniferous magnetite			
New York			
Québec and Ontario			
Tahawas: titaniferous magnetite			
titaniferous magnetite			
Other U. S.			
titaniferous magnetite			
vanadate deposits			
.-•outh America			
Southwestern U. S.			
vanadate deposits			
Peru:			
asphaltite deposits			Large-very Ie:l
			Small
Argentina:			
asphaltite and vanadate deposits			Very large
Venezuela:			
vanadium-bearing crude oils			
Europe and Asia			
Otanma'ki titaniferous magnetite depo.	Q-		
Finland;			
Russi;			
vanadium-bearing mica, vanadium-bearing shale, titaniferous magnetite, sedimentary iron,			Very large
phosphate deposits, coal	0. 1 - 0. 5		Moderate-Lai'Lt
India:			
titaniferous magnetite	0. 5 - 3. 0		
Norway, Sweden, France, Germany:			
titaniferous magnetite, oil shale, sedimentary iron ore			
Union of South Africa:	0. 1 - 0. 4	25,000	Very large
Transvaal titaniferous magnetite deposits			Moderate
South-West Africa:			
Otavi vanadate deposits			Moderate
Northern Rhodesia:			
Broken Hill vanadate deposits			
New Zealand: Fe-Ti-V beach sands			Very large
Australia: iron deposits			Large-very large

(1) Probable semi-quantitative definitions: "Small" = less than 1,000 short tons V2O5; "moderate" = 1,000 to 10, 000 short tons V2Os; "large" = 10,000 to 100,000 short tons V2O5; "\ery large" = m«. c <h •more than 100, 000 short tons \r2°5-

Sandstone Deposits of the Colorado Plateau

Uravan Mineral Belt, Colorado

Vanadium-uranium reserves (excluding "roscoelite" ores I of measured, indicated, and inferred ores estimated for the Uravan Mineral Bell in Colorado (pages 45 to 52) at the end of 1956, 1957, 1958, 1959, and 1960 have been released by the U. S. Atomic Energy Commission:

November 1956 — 4,100,000 short tons

December 1957 — 4,100,000 short tons

December 1958 — 4,400,000 short tons

December 1959 — 4,500,000 short tons

December 1960 — 4,000,000 short tons

These reserve figures for uranium ores, which probably are conservative, average about 1.3 percent Vy03, and at the end of 1960 contained approximately 52,000 short tons of V203.

At the current production rate, approximately 4 to 5 years of reserves were indicated at the close of each of the past 5 years. Obviously the reserve figure at the end of any one year does not truly represent the potential resources of the vanadium-bearing ores. Since potential ores reasonably can be expected to be several times the known reserves, very-large resources of vanadium are indicated for the Uravan mineral belt.

Rifle Creek-Placerville Districts, Colorado

For the "roscoelite type" ores of Rifle and Placerville (pages 52 to 54), developed reserves ranging from 1.25 to 1.75 percent Vo05 total in excess of 500,000 tons and contain approximately 15,000 short tons of Vo05. Potential deposits, mainly in deep deposits, are estimated to be several times the known reserves and represent a large to very large resource of vanadium.

Sandstone Deposits of the Colorado Plateau in Utah, Arizona, and New Mexico

Very large resources of ores with a low-vanadium to high-uranium ratio are present on the Colorado Plateau in Utah, Arizona, and New Mexico (page 54). These deposits are low in vanadium—0.10 to 0.25 percent V^O.-,—but account for about 65,000 tons of reserves of vanadium pentoxide.

Sandstone Deposits of Wyoming and South Dakota

The uranium ores in sandstones flanking the Black Hills in Wyoming and South Dakota (page 55) contain an average of 0.25 percent V_.05, A reserve of approximately 800 short tons of V205 is indicated with only moderate resources.

Organic Shales in the Western United States

Although other organic shales may be important potential sources of vanadium, reserve and resource estimates are available only for the phosphatic shale member of the Phosphoria formation (page 32). Based on a minimum mining thickness of 3 feet, at an average grade of about 0.85 percent V208, reserves of vanadium-bearing shales total about 65 million tons above drainage level. Contained vanadium amounts to approximately 550,000 short tons of V2Og. The vanadium resources, which include inferred reserves and materials below drainage level, are many times the calculated reserves.

Phosphate Deposits of Idaho, Montana, Wyoming, and Utah

Because of complex geologic occurrence, incomplete studies, and economic variables, estimates of total reserves of vanadium in phosphate deposits (page 33) are extremely difficult to determine. The potential resources of the phosphate deposits, in addition to the vanadium in the organic shales of the Phosphoria and other formations, probably can be considered in terms of considerably in excess of 100,000 short tons of v2o5.

Titaniferous Magnetite Deposits of Wyoming

Reserve estimates for the Iron Mountain, Albany County, Wyoming ores (page 27) indicate 12 million tons of high-grade titaniferous magnetite, averaging about 0.6 percent V205 and containing about 72,000 short tons of V205. In addition there is estimated to be approximately 20 million tons of lower grade material containing larger portions of rock-forming silicate minerals. Resources probably would be several times the reserves and would be considered to be very large.

Titaniferous Magnetite Deposits of New York

The crude ore being mined from vanadium-bearing titaniferous magnetite deposits near Tahawas, Lake Sanford area, Essex County, New York (page 27), averages about 34 percent iron, 18 to 20 percent Ti02, and 0.25 to 0.45 percent V205.

Reserves of known deposits are reported to total 121 million tons of titaniferous magnetite ore of which approximately 100 million can be considered available. The total reserves contain about 485,000 short tons of VL>05 and available reserves contain about 400,000 tons of V0O5.

\anadate Deposits of Southwestern United States and Mexico

In recent years there has been no production of vanadate ores in southwestern United States and Mexico (page 55). The total production has been small and potential resources appear to be small.

Titaniferous Magnetite Deposits of Quebec and Ontario, Canada

Titaniferous magnetite deposits associated with gabbro and anorthosite are abundant in the Province of Quebec.40 89 The vanadium content of these ores, averaging between 0.25 and 0.5 percent V0O5, is typical of most other deposits of titaniferous magnetite. The titaniferous magnetite reserve estimates vary from 120 million to 208 million tons and represent very large resources of vanadium. Similar but somewhat smaller deposits are present in the Province of Ontario.

South America

South America has been an important producer of vanadium and still has important resources. In contrast to North American output, most of the South American production and reserves are from asphaltite-type deposits. The Peruvian Minas Ragra deposit has been the important producer, although minor production has been reported from the vanadate deposits of Argentina and Chile. Ash from Venezuelan crude oils also have yielded vanadium.

Asphaltite Deposits of Peru

Although the famous Minas Ragra deposit of Peru (pages 29 to 31) apparently has been almost completely mined out, Peru remains an important potential source of vanadium. It is estimated that the lower grade material surrounding the Minas Ragra deposit and other asphaltite deposits of Peru 38 represents large to very large resources of ore containing 1 to 3 percent V205.

Asphaltite Deposits of Argentina

Because of isolation, scattered occurrence, generally small size, combined with noncompetitive fuel value of the solid bitumens, appreciable amounts of vanadium probably would not be produced from the asphaltite deposits of Argentina (page 31).

Crude Oils of Venezuela

The ash resulting from the burning of the Venezuelan crude oils (page 29) is high in vanadium. These petroleum deposits probably can be considered as a very large resource of vanadium.

Vanadate Deposits of Argentina

Vanadate ores associated with oxidized portions of lead and lead-silver veins have a wide distribution in the Provinces of Cordoba and San Luis. The ore minerals—vanadinite, descloizite, and brackebuschite—line cavities in the oxidized zone. The vanadium content rapidly falls off in depths, and the resources appear to be very small/'*

Vanadate Deposits of Chile

Some vanadate minerals associated with silver-lead and copper deposits have been reported from Chile. Production has been very limited. and the potential resources appear to be very small.

Europe and Asia

Iron deposits of Finland, Sweden, Norway, Russia, and India, and vandiferous shales in Russia and Sweden contain very large quantities of low-grade vanadium-bearing rock. Minor production from the western European nations is derived in part from either steel-plant slags or red muds produced in the extraction of aluminum by the Bayer process.

Finland is the only major European producer of vanadium.

Titaniferous Magnetite Deposits of Finland

The average ore at Otanmaki, Finland, contains about 35 percent magnetite, about 28 percent ilmenite, and about 0.46 percent V205, which is associated with the magnetite (page 28). Representing a very large resource of vanadium, the reserves have been estimated to be approximately 50 million tons of titaniferous magnetite containing about 230,000 short tons of V20;.

Sedimentary Deposits of Western Europe

Under normal conditions vanadium resources in sedimentary deposits of Western Europe probably are not significant. However, France, West Germany, Belgium, Netherlands, Luxemburg, and Italy derive a part of their vanadium supplies from either steel-plant slags or red muds produced in the extraction of alumina by the Bayer process.

Vanadate Deposits of Spain

Spanish ores supplied the vanadium from which Kent Smith produced the first button of ferrovanadium.00 Although at one time a large proportion of the world's supply came from near Zafra, Spain, production never was large. Ore minerals, vanadinite and descloizite, were found in the oxidized portion of lead veins that cut vanadium-rich clays. Potential resources are small.

Vanadium Deposits of Russia

Although little is known of Russian vanadium deposits, the resources of vanadium may be extremely large. Shimkin 01 mentions two general types of deposits—a roscoelite type and vanadium-containing iron deposits.

The Kara-Tau vanadium-mica ore-body in Turkestan is reported to be of great size. It has been traced for 25 to 30 kilometers, and its thickness ranges from 10 to 15 meters. Metamorphism of sedimentary beds has resulted in thin bands of roscoelite alternating with bands of flint. '

A titaniferous magnetite deposit at Kusa in the Urals, associated with metamorphosed gabbro intrusives is reported to contain an average of 0.35 to 0.50 percent vanadium, 12.5 to 14.2 percent Ti02, and 46.2 to 54.4 percent iron. A similar deposit at Pervoural'sk, also in the Urals, contains 0.2 percent V20.-, with 2 percent Ti02, and 17.9 percent iron. Both deposits are reported to contain about 50,000 tons V20s.

Very large vanadium resources also are reported at the Kerch iron mine in the Ukraine. The vanadium content of the ore is about 0.07 percent, but the enormous size of the deposit, according to Shimkin, indicates a total of about 2 million tons of V203.

Titaniferous Magnetite Deposits of India

Titaniferous magnetite deposits of India near the southern border of the Dhalbhum subdivision of Singhbhum and extending into Mayurbhanj; near Nuasahi in Keonjhar; and in Orissa north of Godasahi, Nilgiri, and in the Keonjhar district are reported to contain 0.5 to 3 percent V2Oj. These deposits,85 02 93 associated with basic and ultra-basic rocks, represent moderate to large vanadium resources.

Beach Sands of Japan

During World War II an undisclosed amount of vanadium was produced from beach sands of Japan which had been derived from the breakdown of titaniferous magnetite deposits.

Africa

Vanadate ores of South-West Africa and Northern Rhodesia have been important sources of vanadium. Vanadium now is being recovered from the potentially important titaniferous magnetite deposits in the Union of South Africa.

Titaniferous Magnetite Deposits of the Union of South Africa

In the Bushveld Complex, Transvaal, Union of South Africa, a 3-foot band with a unitorm composition of 1.25 percent V20.-, has been estimated by Schwellnus and Willemse34 to contain a possible 1 million tons of V20,> One property in the Complex has been reported:ir' to have an estimated reserve of 25,000 tons of V20.-,. These undoubtedly are conservative estimates.

Vanadium-bearing titaniferous magnetite resources of the Union of South Africa are very large.

Vanadate Deposits of Union of South Africa (Transvaal)

Minor occurrences of vanadinite and descloizite have been found in oxidized zones associated with deposits of lead in the Union of South Africa, but the potential resources appear to be very small.3*

Vanadate Deposits of South-West Africa

Although the 1960 production of 1,500 short tons of recoverable V2O3 is the highest recorded from the vanadate deposits of the Otavi Mountains, South-West Africa (page 55), resources are considered to be only moderate.

Vanadate Deposits of Northern Rhodesia

From 1922 to 1955, Northern Rhodesia supplied about 5 percent of the world's vanadium. With the gradual depletion of the oxidized ores of Broken Hill (page 56), and the developing importance of other sources of vanadium, Northern Rhodesia's production has been of less importance to the world's reserve picture. Potential resources are only moderate.

Oceania

Iron deposits of Australia and titaniferous magnetite beach sands of New Zealand represent large to very large potential resources of vana-

USES

Markets

The ultimate user of most vanadium products is either the steel or chemical industries. A partial list of uses of vanadium are given on pages 66 to 74. The major producers and purchasers of vanadium ores are integrated companies in that they not only extract the vanadium from its ores, but they also prepare the vanadium for use by the ultimate consumer which may be as the pure element, an oxide, an alloy additive with iron, aluminum, titanium, chromium, etc. The small number of purchasers of intermediate vanadium products in the United Slates must be considered somewhat of a deterrent to the relatively small, independent producer.

Several essential factors influence the vanadium market."[4] In recent years, the amount of vanadium used in a ton of steel has been increasing. A factor that distinguishes the vanadium market from one similar to the copper market is that very little vanadium is recovered as scrap. Upon remelting, the vanadium goes into the slag and does not return to the industry. Also in its use as a catalyst much of the vanadium is lost.

Of utmost importance in the present and projected vanadium markets is the potential availability of an almost unlimited industrial supply of vanadium. Under present economic and technological conditions, certain domestic and foreign resources are not economical, but with either an increase in price or a change in technology, other large vanadium-bearing deposits could be brought into production.

The close chemical relationship of vanadium with molybdenum, columbium, tantalum, and tungsten could have an important bearing on future vanadium markets. In certain cases the presence of vanadium in alloys containing another element enhances the properties of the other alloy material; also to a certain extent vanadium is a satisfactory substitute for other alloying materials. This latter factor particularly is true with regard to molybdenum. Because vanadium and molybdenum impart similar qualities to steel, under suitable economic conditions vanadium could be an important substitute for molybdenum in the steel industry.

Applications

Current metallurgical and chemical application of vanadium is based on four primary chemical compounds produced during the milling and extraction of vanadium-bearing ores:

1. Vanadium Pentoxide, Technical, Fused

   This material is also referred to as "Fused Oxide" and "Fused Black." Two grades of the fused oxide are being produced.

   a. 88 to 92 Percent V_2O_5

      This product is made by the fusion of an intermediate sodium hexavanadate (red cake) compound. Because this material is formed by the fusion of an alkali salt, the principal contaminant is sodium. The sodium content of the fused oxide is equivalent to approximately 8 percent Na_2O, with some potassium also present.

   b. Plus 98 Percent V_2O_3 (Low Alkali)

      This low-alkali fused oxide is produced by the decomposition and fusion of ammonium meta- and poly-vanadate intermediate compounds. This substance, marketed in the United States since about 1958, is one of the newest and most recent vanadium products.

2. Vanadium Pentoxide, Technical, Air Dried
   This product, commonly referred to as "red cake," is the dried but unfused sodium hexavanadate. Theoretically sodium hexavanadate (Na2H2V0O17) contains 87.2 percent V20.-„ but the commercial product usually has 83 to 86 percent V20.-,.
3. Ammonium Metavanadate, Technical
   This vanadium compound, usually referred to as "AMV," has a minimum grade specification of 99 percent NH4VO3. The product is made by redissolving red cake in an alkaline or ammoniacal solution and crystallizing the AMV by the addition of excess ammonium chloride. Ammonium metavanadate can also be produced via a solvent-extraction process using tertiary or quarternary amine liquid ion exchange reagents.
4. Vanadium Pentoxide, Purified
   The purified vanadium pentoxide has an equivalent V205 content of about 99.6 percent. This compound is produced by calcination of ammonium metavanadate.

These vanadium compounds are the basic raw materials used for making ferrovanadium, vanadium metal and nonferrous alloys, vanadium catalysts, and the variety of vanadium chemicals used in industry.

Ferrous Alloys

Vanadium is introduced into the various types of alloy steels in the form of ferrovanadium. Between 80 and 90 percent of the domestic consumption of vanadium has been used in steel making, mainly in the form of ferrovanadium alloys. Table 8 shows four grades of ferrovanadium allovs currently available in the United States.11''

TABLE 8

FERROVANADIUM ALLOYS

Iron- Foundry Grade	Vanadium	38 to 42%
	Silicon	7 to 11%
	Carbon	approx. 1.0%
Grade A (Open Hearth)	Vanadium	50 to 55%
	Silicon	maximum 7.5%
	Carbon	maximum 2.0%
Grade B (Crucible)	Vanadium	50 to 55% + 70 to 80%
	Silicon	maximum 2.25%
	Carbon	maximum 0.5%
Grade C (Primos)	Vanadium	50 to 55% + 70 to 80%
	Silicon	maximum 1.25%
	Carbon	maximum 0.2%

Almost all of the ferrovanadium produced in the United States is manufactured by the electric-arc reduction of fused vanadium pentoxide. Carbon, silicon, and aluminum are used as reducing agents. The electric-arc furnaces must be designed to produce conditions for an almost instantaneous reaction because high temperatures are necessary for the reduction of vanadium and because the metal reoxidizes very easily at these temperatures.

The aluminothermic method of producing ferrovanadium, first used in the American metal industry in 1907, is still practiced extensively in many countries. Indirect information indicates that the low-alkali fused vanadium oxide may have more advantage in the aluminothermic process than it does in the electric-furnace method. Apparently vanadium losses are minimized if the low-alkali fused vanadium oxide is used.

The two main reasons for using vanadium in steel are to control and reduce grain size and to increase the temperature stability of the steel. Many of the desirable properties which vanadium imparts to steels are associated with the unique properties of the vanadium carbides. Merrill 9i' states that vanadium is thought to strengthen and harden steel by providing a fine almost submicroscopic dispersion of vanadium carbides. With proper vanadium additions, a uniform fine-grain structure can be obtained in large forgings even though they must be cooled slowly during heat treatment because of their size.

Nearly all tool steels contain vanadium. This preference for vanadium is based on the wear resistance, high hardness, and temperature stability of the vanadium carbides. The tendency for vanadium carbides to coalesce in the 1000° to 1200 °F range is considerably less than for most other alloy carbides. This desirable characteristic permits the use of higher working temperatures because the tendency for softening is minimized.

Sprankle °6 has listed the following major applications for vanadium in steels:

"1. Tool steels use large quantities of vanadium for grain-size control for guaranteed depths of hardening and toughness after heat treatment. Vanadium content in the low alloy type tool steels ranges from 0.10 percent to 1.0 percent, but generally is 0.20 percent to 0.40 percent V. The usual tool-steel classification includes water hardening, hot-work, and special-purpose grades. Such applications as hand tools, wrenches, punches. chisels, and hot work die steels are typical examples.

"2. High speed steels are another broad classification of tool steels where larger quantities of vanadium are used for highest wear resistance, retention of cutting edge, and as a grain growth inhibitor. Originally, the well-known 18-4-1 (18W-4Cr-

IV) and the 14-4-2 (14W-4Cr-2V) were the most popular types for high speed cutting. Recently, the 6-6-4-2 (6W-6Mo-4Cr-2V) has become most popular in the United States. For increased wear resistance, carbon and vanadium are both increased to take advantage of the formation of the extremely hard vanadium carbide.

"3. In the constructional alloy grades of steel, vanadium is used as an alloy addition to improve mechanical properties. Due to fine dispersion of undissolved carbide at normal quench temperatures, the low-alloy type of vanadium steels show greater yield to ultimate strength ratios. This, in many cases, is of the order of 20,000 pounds per square inch higher in the vanadium-containing steels.

"Another desirable feature is that the relative insolubility of vanadium carbide in quenched and tempered steels allows higher tempering temperatures to attain the same strength level as their nonvanadium-bearing counterparts. This quite unique property of vanadium results in considerable improvement in toughness or ductility of steels.

"4. In high temperature steels, the carbide stability of vanadium carbide at elevated temperatures contributes to improved creep resistance. Chromium-molybdenum-vanadium types with approximately 0.25 percent V are commonly used for high-temperature bolting steels. The broad classification may include steels from 0.2 percent to 0.5 percent carbon and 0.2 percent to 0.4 percent vanadium, usually combined with other carbide-forming elements such as molybdenum and chromium. These steels, when suitably heat treated, show marked resistance to movement or stretch up to 1,000 F.

"5. Cast steels show the same advantages with vanadium additions as wrought products. In addition, the decrease on dendritic growth in castings is an added advantage in the use of vanadium. Vanadium contents ordinarily range from 0.05 percent to 0.20 percent, even up to as high as 0.50 percent vanadium, usually added with other alloying elements. Typical steel-casting compositions are (1) 0.35 percent C, 0.2 percent V, for locomotive motor frames, heavy gear housings, etc.; (2) 1.5 percent Mn, 0.1 percent V, for transportation equipment; (3) 1.5 percent Ni-0.1 percent V, for heavy equipment dies; and (4) 1.0 percent Mo-0.2 percent V, for large turbine castings.

"6. Vacuum melted steels are becoming increasingly important and require special preparation of ferro-alloys in the melting of extremely high-quality steels. Although this development is in its infancy, the demand for special-purpose steels for supersonic aircraft, missiles, and atomic energy requirements. has imposed restrictions on impurities and gas content of an extremely high order. New techniques of ferro-alloy manufacture. including vacuum melting of vanadium metal of high purity, are under way to meet this challenge."

Vanadium Metal and Non-Ferrous Alloys

Although Marden and Rich1 had succeeded in producing ductile vanadium metal in 1929, not until 1950 was a method developed which could produce pure vanadium in massive form and in sufficient quantities for potential industrial or military applications. This process developed by McKechnie and Seybolt 9T is based on the calcium reduction of vanadium pentoxide in the presence of iodine. The purified vanadium pentoxide, calcium metal, and iodine are charged into a thickwalled steel vessel. The reaction vessel is sealed, and the reaction is initiated by the application of heat in an induction furnace. The reaction is rapid. and within a few seconds a regulus or button of vanadium has collected in the bottom of the bomb. The button or regulus that is formed is not suitable for fabrication and must be remelted in a consumable-electrode vacuum-arc furnace. The ingots from this remelting are used in the fabrication of bars, plate, foil, or wire. Very high temperatures and pressures are reached during the short reaction period.

The iodine addition provides improved energy relationships over the calcium chloride flux used by Marden and Rich and also permits a clean separation between the molten vanadium metal and the slag that is formed.

The vanadium metal that is produced by industrial modifications of the calcium-iodide reduction technique has a minimum chemical analysis of about 99.7 percent V. Table 9 lists typical analyses of industrial vanadium metal.

The process developed by McKechnie and Seybolt was a major step in transposing vanadium metal from essentially a laboratory curiosity to metal of high industrial potential.

Merrill 'J0 Br' °8 Schaufus 10° Kinzel101 and others have discussed the details of vanadium fabrication. The general procedures of vanadium fabrication include remelting, hot working, cold working, extrusion. welding, and machining.

Pure vanadium metal is very ductile and a 99-percent reduction by cold rolling without annealing is possible. Hot working of the metal also is not difficult, but the metal surface must be well protected during heating by inert atmospheres or other means if surface contamination is to be avoided. Vanadium does not show any phase transformation during heating or cooling, but the remelting and hot working requires protective

TABLE 9

TYPICAL COMPOSITIONS OF INDUSTRIAL

HIGH-PURITY VANADIUM METAL

No. 19S	Vanadium	99.7%.
	Oxygen	0.10%
	Nitrogen	0.04%>
	Hydrogen	0.008%,
	Iron	0.04%
	Carbon	0.03 %
No. 2-°	Vanadium	99.8 to 99.9%
	Oxygen	0.05 to 0.12%
	Nitrogen	0.02 to 0.04%
	Hydrogen	0.001 to 0.004%
	Carbon	0.03 to 0.07',
No. 3 -"	Vanadium	99.7 to 99.8%
	Iron	0.10%o
	Carbon	0.10%
	Silicon	0.05%
	Nickel	0.005%
	Chromium	0.01 %

atmospheres because the hot metal oxidizes rapidly when exposed to air. The oxidation forms V20., which penetrates the surface as small fingers which form perpendicular to the metal surface. This nonuniform oxidation causes embrittlement of the surface; the small fingers of V205 also act as stress risers and reduce the effective strength of the metal.

Vanadium metal cold works well if the surface is free from contamination. If the surface of the metal is oxidized, special machining techniques are used to remove the surface layer before cold working. Extrusion of vanadium works well at temperatures under 1,000°F. This procedure eliminates the troublesome heating step for hot working, and 'warm" extrusion followed by cold working appears to be an economical route for vanadium fabrication. The ductile metal has a machinability approximately equivalent to that of the more difficult stainless steels. Vanadium also can be successfully welded if precautions are taken to shield the molten metal and adjacent zones from oxidizing conditions.

A list of the phvsical properties of vanadium metal is given in Table 10.

TABLE 10-"

Physical Properties of Vanadium Metal

Atomic number	23
Atomic weight	50.95
Reported isotopes	46, 47, 48, 49, 50, 51, 52. 53.
Crystal structure (to 1550 ± 10°C) (2822°F)	Body-centered cubic
Lattice constant	3,034
Density (g/cc)	6.11
Melting point	1900° ± 25°C (3452°F), 1919 ± 2°C (3486°F)
Boiling point	3000°C (5432°F)
Vapor pressure (1393-1609°C) (2539-2928°F)	R In p = 121.95 x 103T!— 5.123 x 10-4T + 36.29 R = gas constant (cal mob1 deg"11 p = pressure in atmosphere In = logarithm to base e T = absolute temperature (° K)
Volatility at melting point	Very low
Specific heat (20-100°C) (68-212°F) (cal/g)	0.120
Latent heat of fusion	4 kcal/mole
Latent heat of vaporization	106 kcal/mole
Enthalpy (25°C) (77°F) (kal/mole)	1.26
Entropy (25°C) (77°F) (cal/ mole/°C)	7.05
Thermal conductivity (cal/sq cm/ : C/cm)	
100°C (212°F)	0.074
500 C (932° F)	0.088
700 C (1292°F)	0.084

Physical Properties of Vanadium Metal

(continued)

Electrical resistance (20°C) (68°F) (microhm-cm)	24.8
30.6 DC (87 F)	25.2
58.9°C (138°F)	27.4
Temperature coefficient of resistance (microhm-cm/°C)	
0-100°C (32-212 °F)	0.0034
0-200°C (32-392°F)	0.0033
Thermal emf versus platinum cold junction (0°C (32 F) (my)	
100°C (212°F)	0.63
200°C (392° F)	1.56
400°C (752°F)	3.97
700°C (1292F)	9.26
900°C (1652°F)	13.97
1000°C (1832°F)	16.71
Magnetic susceptibility	1.4 x 10° (cgs)
Superconductive transition temperature	5.13 K
Coefficient of linear thermal expansion	9.7 – 0.3 x 10"°/°C x-ray (20-270 C) (68-1328°F)
	8.95 x 10-VoC dilatometer (200-1000 C) (392-1832°Fi
Thermal expansion (in/in/°C)	
23-100°C (73-212°F)	8.3
23-500°C (73-932GF)	9.6
23-900°C (73-1652°F)	10.4
23-1100°C (73-2012°F)	10.9
Recrystallization temperature	700-800CC (1292-1472 °F) (for 70% cold-rolled sheet)
Modulus of elasticity	18 to 19 x 10° psi
Shear modulus	6.73 x 10° psi
Poisson ratio	0.36
Thermal neutron-absorption cross section (barns/atom)	4.98 ± 0.02

Vanadium is also being used as an alloying agent in nonferrous metals. Both the aluminum and titanium metal industries use vanadium as an alloying element, and several grades and types of master alloys are being produced for these industries. Vanadium-aluminum alloys containing from 2.5 to 5 percent vanadium are used as additives for the control of thermal expansion, electrical resistivity, and grain size in both wrought- and cast-aluminum metal parts.

Master alloys for the production of special titanium metal alloys are also available. These vanadium-aluminum master alloys contain between 40 to 85 percent vanadium.

Vanadium Catalysts and Chemical Compounds

Approximately five to six percent of the domestic vanadium consumption is applied directly in the form of various vanadium compounds. Manufacturing of oxidation catalysts for the chemical industry is the largest single application of vanadium compounds.03 The basic raw materials for the production of these catalysts are ammonium metavanadate and purified vanadium pentoxide. Some vanadium catalysts, such as those used in the sulfuric acid industry, are compounded by manufacturers specializing in producing catalysts, but many of the catalysts used in the organic chemicals industry are made by companies that use them.

The application of vanadium compounds as catalysts has been studied extensively. Cosman 10> has published a bibliography of over 300 references on vanadium catalysts. These references were compiled from the chemical abstracts and cover the years 1940 through 1954. Some of the current applications of vanadium catalysts in the chemical industry are as follows:103

(1) The manufacture of sulfuric acid
(2) Oxidation of benzene to maleic anhydride
(3) Oxidation of naphthalene to phthalic anhydride
(4) Oxidation of anthracene to anthraquinone
(5) Oxidation of chlorinated hydrocarbons to maleic or fumaric acid
(6) Oxidation of acrolein to acrylic acid
(7) Oxidation of toluene to xylene
(8) Oxidation of alkenyl and alkyl derivatives of pyradene in the presence of ammonia
(9) Oxidation of amino acids
(10) Oxidation of cyclohexanol to adepic acid
(11) Oxidation of napthalene to 1, 4, naptho quinone
(12) Ammonia synthesis

(13) Hydrogenation of CO
(14) Dehydration of organic acids to ketones
(15) Dehydrocyclization of paraffin to aromatics such as hexane to benzene
(16) Dehydrogenation of butane to butenes
(17) Dehydrogenation of butenes to butadiene
(18) Oxidizing agent in the formation of aniline dyes
(19) Catalyst in petroleum cracking

The use of vanadium catalysts for completing the oxidation of irritating and smog-producing hydrocarbons in automobile exhaust fumes is being studied. This application is probably one of the newest being considered for vanadium catalysts, which are often viewed as key process reagents.

Vanadium compounds are used in a variety of other industrial applications.

Sodium vanadate has proved to be a good corrosion inhibitor in certain types of gas-scrubbing systems. The addition of NaV03 has been quite effective in scrubbing systems where weak acids such as carbonic acid are formed during the scrubbing operation.

Vanadium has been used in ceramics both as an actual component of refractories and as a coloring material. Ceramics composed of AI0O3 plus V203 have been used to produce electrical resistors sensitive to temperature changes.[104] These thermostances have good shock resistance, moderate thermal expansion, and high thermal conductance.

Vanadium has been used in the production of a wide variety of ceramic colors.[104] Combinations of lead oxide, zirconia, and vanadium salts produce yellow colors; and blue to bluish-green shades are made by combining zirconia, silica, and vanadium pentoxide. Other yellow colors which have been used for glazes, underglazes, or body stains are obtained by combining tin oxide and V205. A bright-red refractory ceramic material is produced when V20.-„ Se and Cd are combined.

Vanadium added to glass produces a practically colorless glass that cuts out nearly all radiation in the ultraviolet range. Vanadium-bearing glasses are being considered for use in containers to prevent the loss of the vitamin content of fruit juices by action of ultraviolet or actinic rays.

Vanadium compounds have also been used in photography, medicine. and as a drying agent in paint manufacture.

The broad scope and wide variety of applications illustrate the versatility of vanadium and also indicate that new uses will undoubtedly be found for this complex element. Colorado has very large resources of vanadium, but to maintain its lead as the principal producer, the state must continue studies that will lead to reduction in mining and metallurgical costs.

COLORADO PROCESSING HISTORY

The history of mining and milling of vanadium in Colorado coincides closely with the state's production of radium and uranium. Although some of the plants which processed the roscoelite-type ores produced only vanadium, most of the mills have treated the carnotite-type ores because the metallurgical and economic aspects of processing these complex ores have been interdependent. The mining and milling operations on the carnotite and roscoelite ores have passed through a number of phases in which the relative importance of the vanadium, uranium, and radium products varied.

The first shipment of high-grade carnotite ore from the Colorado plateau area was made in 1898, and during the next 10 to 12 years apparently the objectives of the mining and milling operations differed at times. The initial mining and milling installations were designed to produce uranium and vanadium. The uranium was purchased by manufacturers of ceramics and glass where it was used as a coloring agent.[103] The Curies discovered radium in 1898, and by the early 1900's some Colorado high-grade carnotite ores were shipped to France for radium extraction. Most of the early Colorado milling processes, however, were not designed to recover radium, and the element passed on through the circuits. The radium was principally associated with the slime portion of the tailings. By 1911, some "radium-bearing slime" concentrates were being shipped.[106] Radium production increased rapidly and the Encyclopaedia Britannica states that between 1913 to 1923, the United States was the leading producer of radium. Nearly all of the radium-bearing concentrates used for this production came from the Colorado Plateau area, and during this period vanadium and uranium were primarily considered to be by-products.

After the high-grade deposits of pitchblende in the Belgian Congo came into production in 1922, United States radium production dropped off rapidly, and vanadium again became the major product from the milling operations.

During the early part of 1942, the Army Corps of Engineers started to produce uranium for the Manhattan project, and gradually vanadium again became a by-product of the Colorado Plateau milling operations.

The vanadium production from the Colorado mills has not been continuous, and several slumps in production have occurred. Undoubtedly. the relative preference for the production of vanadium, uranium, and radium at individual mills may have varied from the over-all trends which have been outlined in the preceding paragraphs. Types of ore, reagent availability, transportation, and many other factors have influenced the flowsheets that have been used in both early-day and present milling operations.

Early Processes and Operations

Kimball[107] has stated that the first shipments of carnotite ore from Colorado were sold to Charles Poulot in 1898. Poulot, a Frenchman who had come to the United States to locate ores of rare metals, was particularly looking for uranium-bearing materials. In 1900 he joined with F. Voilleque and constructed an experimental plant in the La Sal Creek area of Western Montrose county.[108] The experiments were successful. and about 120 tons of concentrates were produced. In 1901 together with Mr. James McBride, Poulot and Voilleque formed the Rare Metals Mining and Milling Company, and near the present location of Slick Rock, Colorado, built the first vanadium-uranium mill that was operated in the Colorado Plateau area.

Lake and Lundquist[109] have described the early vanadium-uranium operation of the Colorado area, and Table 11 presents data they compiled on the milling operations of the Colorado Plateau. Several additional plants not on the original table are also listed.

The operations of the Rare Metals Mining and Milling Company plant are described in detail by Fleck and Haldane.[108] A block-type flowsheet is shown in Figure 5. The vanadium and uranium values were extracted by an acid-leach process. The ore was crushed by hand to about a minus-three-inch size and dry ground to pass a 40-mesh screen. The ground ore was mixed with water and sulfuric acid, and the slurry was stirred by hand with wooden paddles. The acid addition was about 50 pounds per ton of ore. The pregnant liquor plus the slimes were decanted and precipitated with sodium carbonate. The precipitate was allowed to settle and then collected on a sand filter. The product was air dried and sacked for shipment. Normally the product was yellow and contained about 12 percent U_3O_8 and slightly over 12 percent V_2O_5.

The Rare Metals operations were transferred to the Western Refining Company in 1903 and then to the Dolores Refining Company in 1904. Both of these companies used the Haynes-Engle carbonate-leach extraction procedure.[108, 110] Figure 6 shows a simplified flowsheet of the Haynes-Engle process.

The ore was dry ground to minus-14 mesh and boiled with a 10-percent solution of sodium carbonate. The uranium and part of the vanadium were precipitated by adding sodium hydroxide. This product containing about 85 percent U_3O_8 was filtered and dried. The vanadium in the filtrate was precipitated as a calcium vanadate by adding milk of lime. The barren filtrate was either discarded or recarbonated with carbon dioxide, and recirculated to the leaching operation.

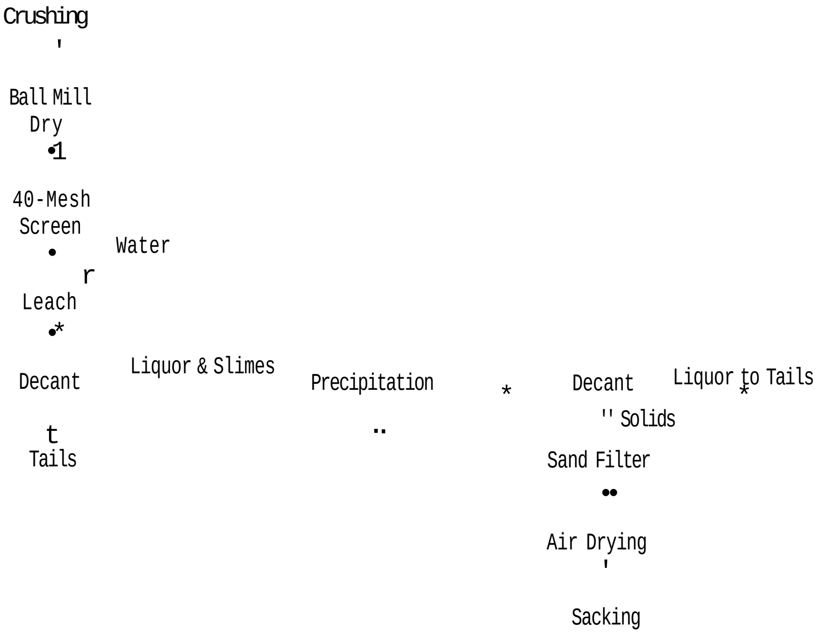

Figure 5—Rare Metals Mining and Milling Company Mill
McIntyre District 1900-1902

The American Rare Metals Company, the successor of the Dolores Mining Company, used an acid-leach process which produced both a uranium-vanadium product and a radium-slime concentrate. Figure 7 illustrates the flowsheet that was used.109 106 The finely crushed ore was leached with sulfuric acid. This leach dissolved much of the uranium, vanadium, copper, and iron contained in the ore. The clear liquor was decanted from the solids, and sulfur dioxide was added to reduce the vanadium and iron to the ferrous and vanadyl forms. Calcium sulfate was precipitated by adding lime and this material was separated from the liquor by decantation. The precipitation was completed with additional limestone. and a concentrate containing approximately 20 percent U_3O_8 and an equivalent amount of V_2O_5 was obtained.

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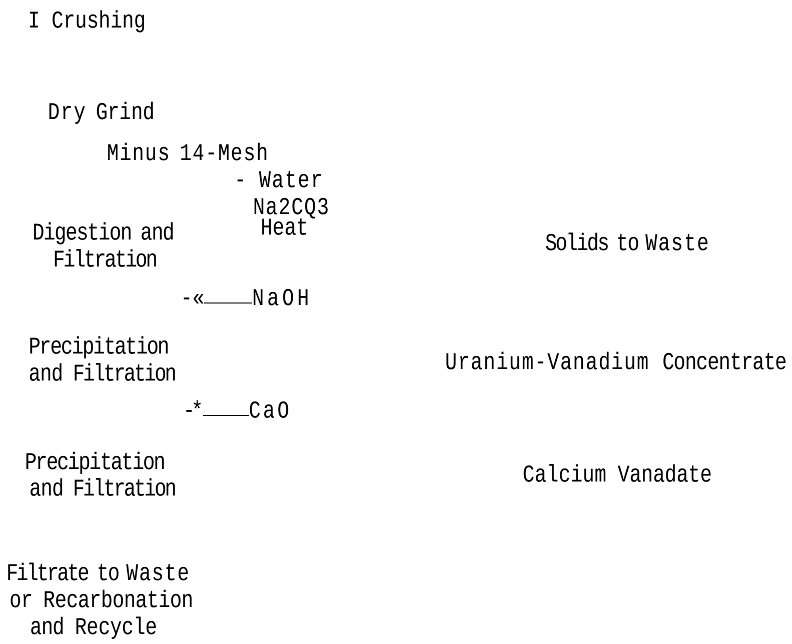


Figure 6 — Haynes-Engle Process

The radium was contained in the slimes fraction of the acid-leached residue. These slimes were recovered by classification and air dried. A product carrying as high as 100 milligrams of radium per ton was produced.

The first salt-roast plant on the Colorado Plateau was built by the Primos Chemical Company at Newmire, Colorado. This plant which processed the roscoelite ores of the Placerville district operated intermittently between 1910 and 1922. Figure 8 is a flowsheet showing the various steps of the Primos operation.[109] [106]

The ore was mixed with salt and coarsely ground. The mixture was then dried to about 1-percent moisture and reground to minus-20 mesh. This ore-salt mixture was roasted for about three hours, and the calcine

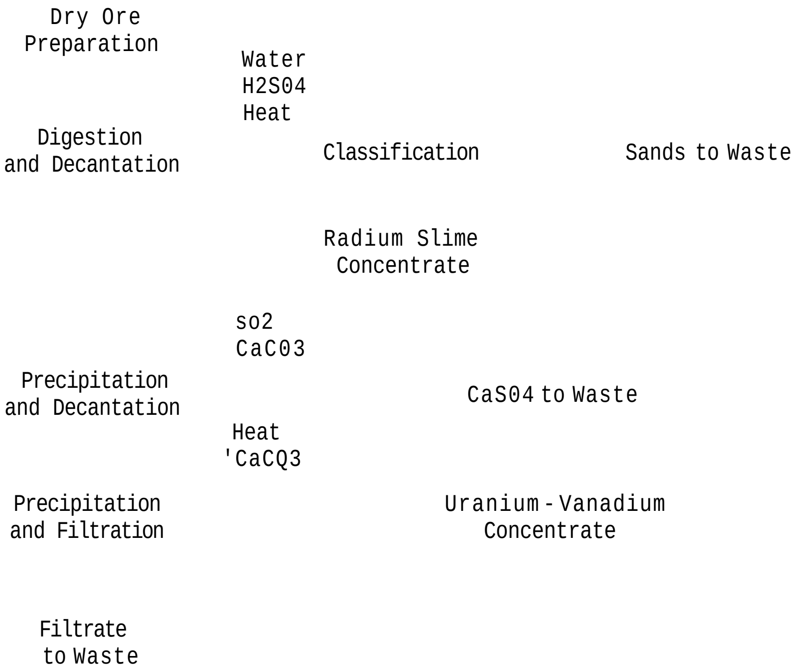


Figure 7 — American Rare Metals Company Flowsheet
McIntyre District (Slick Rock) 1912

was leached with water. The vanadium which was converted to sodium vanadate during the roasting operation was readily soluble in water. The solutions were recovered from the leach slurry by filtration, and the vanadium was precipitated as an iron vanadate by the addition of ferrous sulfate. The iron vanadate was filtered, dried, and packed for shipment to Primos, Pennsylvania, where it was reduced to ferrovanadium by the Goldschmidt aluminothermic process.

Early accounts of the initial Primos operation indicate that partial volatilization of the vanadium during the roasting operation was a prob-

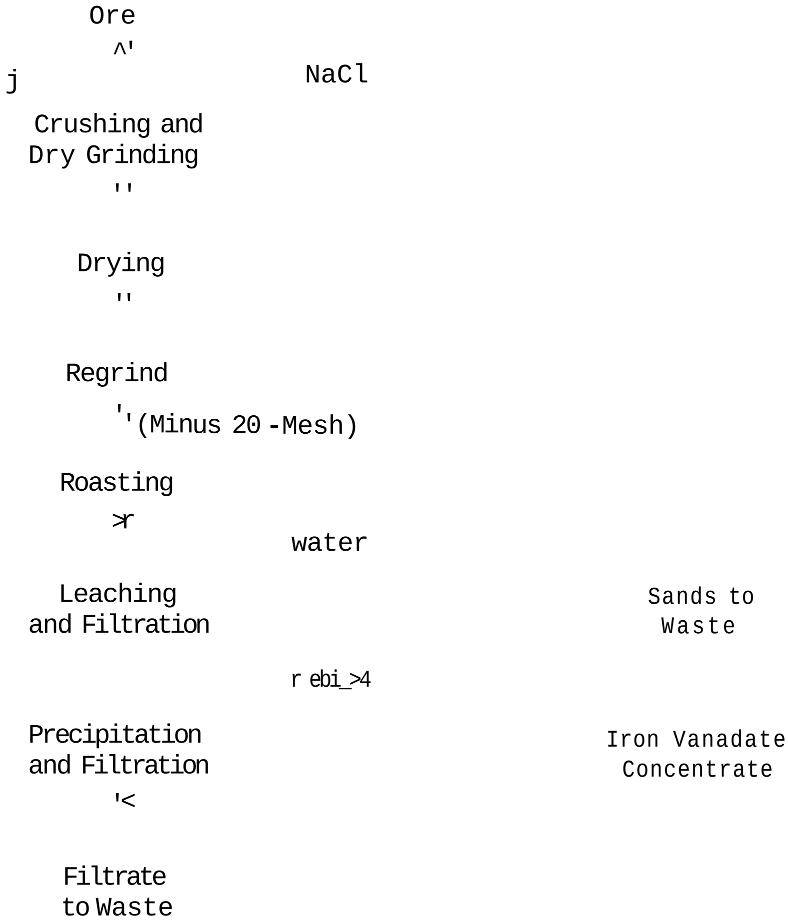


Figure 8 — Salt-Roast Flowsheet

Primos Chemical Company

Newmire, Colorado — 1910 to 1922

lem, an effect that may have been caused by a combination of reducing conditions and an essentially dry atmosphere in the roasters. Apparently, however, the problem must have been solved after a relatively short period of operation.

The Standard Chemical Company operated a 50-ton-per-day upgrader at the site of the present Uravan plant. This operation which was known as the Joe Junior Mill operated intermittently from 1915 to 1923 and produced significant quantities of a concentrate containing about 4 percent U308 and 12 percent V0O3. A wet sand-slime separation was used to produce the concentrate, which was dried and shipped to the Standard Chemical Co. plant in Pennsylvania where the uranium, radium, and vanadium were separated in a rather complex process.

Developments Between 1924 and 1940

After 1924 the vanadium and uranium flowsheets gradually became more complex. The circuits also were changed constantly, and many combinations of the basic acid-leach, alkaline-leach, and salt-roast processes were used. Following are some of the reasons given for rapidly changing process methods:100

1. Varying demands over the years for vanadium, uranium, and radium values.
2. Tightening of specifications on final products.
3. Normal quest for improved recovery and lower costs.
4. Constant improvement of processing equipment.
5. Widely varying character of the vanadium-uranium ores of the Colorado Plateau area.

As an example of the evolution of vanadium processing, Lundquist and Lake have given the following account of changes which took place at the North Continent Mines Company plant at Slick Rock, Colorado.10i)

> "The first North Continent plant was built in 1934 and the process, as shown in Figure 9, was patterned after the operations of the Shattuck Chemical Company in Denver. This company- was treating carnotite ore on a limited scale by use of a patented 'acid cure' process, which was developed by J. S. Potter, Manager of the company. The North Continent Mines Company was formed by the W. A. Baehr organization of Chicago, which also controlled the Shattuck Chemical operations.
>
> "In the first flowsheet, the ground ore was mixed with concentrated sulphuric acid and water, and the mix allowed to cure for about 24 hours in order to render soluble both the uranium and vanadium values.
>
> "The cured mass was broken up, pulped with water, and then classified by means of a counter-current classification-wash step.

The insoluble radium-bearing slimes and soluble vanadium and uranium values were removed in the overflow and the sand rake product sent to waste. The radium concentrates were recovered and washed in a filter press, then dried and shipped to the Shattuck Chemical Company in Denver for final treatment. The acid leach liquor was evaporated in lead-lined vessels and steam-jacketed kettles to near dryness. The solid residue was then roasted in a reverberatory furnace at 1200° F. for conversion of the vanadium sulphate to iron vanadate. The soluble uranium and aluminum salts in the calcines were dissolved in water and

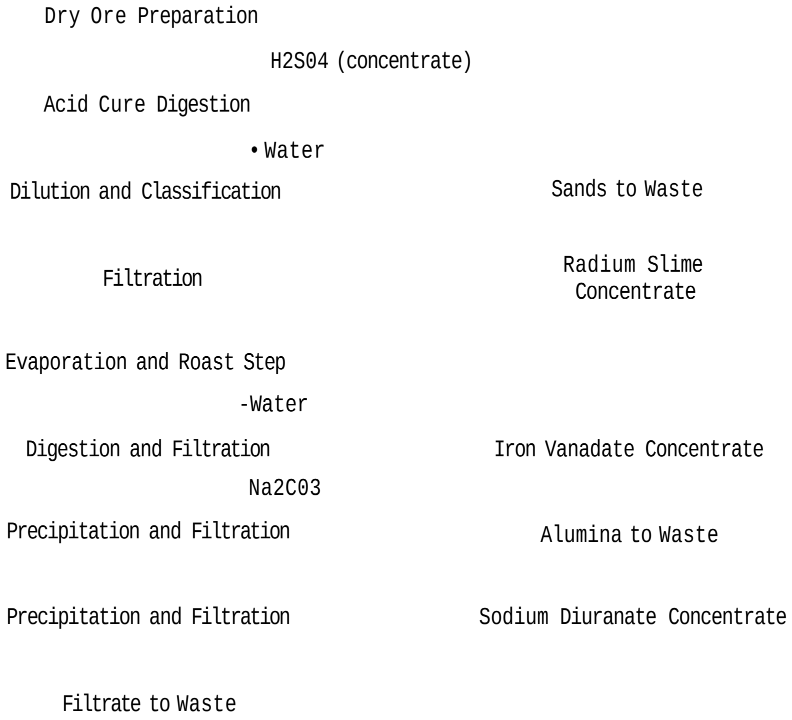


Figure 9 — North Continent Mines Company (Circuit 1)

the insoluble iron vanadate separated and washed in a filter press. The iron vanadate was dried and later converted to ferro-vanadium by the Alumina Exothermic process. A waste aluminum hydroxides product was then precipitated from the filtrate by pH adjustment with soda ash. Following the clarification of this liquor, a low-grade uranium concentrate was precipitated with caustic soda. This product was converted to uranyl acetate or uranyl nitrate by dissolving in the corresponding acid and crystallizing the uranium salts.

"The second modification of the acid cure process practiced at Slick Rock included a vanadic acid precipitation step for vanadium recovery, as shown in Figure 10. In this step, the vanadic acid was precipitated by proper pH adjustment of the boiling solution after the addition of an oxidizing agent. The vanadic acid was fused into the commercial vanadium product. The uranium-bearing filtrate was partially neutralized with soda ash to produce a ferric sulphate which was filtered off and discarded. The filtrate was neutralized with caustic soda and a low-grade uranium precipitated. This product was further refined by redigesting in sodium carbonate solution and evaporating to crystallize a sodium uranyl carbonate salt.

"A major change was again made in the flowsheet in 1941 by adoption of a combination salt roast, water leach, and acid leach process, as shown in Figure 11. In this combination of steps, part of the vanadium was extracted in the water leach circuit, while additional vanadium and all of the uranium was recovered in the acid leach circuit. The two liquors obtained were clarified and combined to produce a vanadic acid salt after oxidation and hydrolysis. The red cake was fused for shipment. The uranium-bearing filtrate was treated with soda ash for precipitation of a waste alumina cake, and the uranium was recovered by precipitation from the filtrate with the addition of caustic soda."

A good deposit of the roscoelite vanadium ore was discovered near Rifle, Colorado, in 1909. Development of this deposit was started in 1921. and in 1924 a mill was built at Rifle, Colorado, to process the ore. In 1926 the property was sold to the Union Carbide Corporation and was operated by the United States Vanadium Company, a subsidiary of the parent corporation. The mill was shut down in 1932, but was reactivated in 1942.

The Rifle mill was the second salt-roasting operation in Colorado. and the flowsheet was similar to that of the Primos Chemical Company

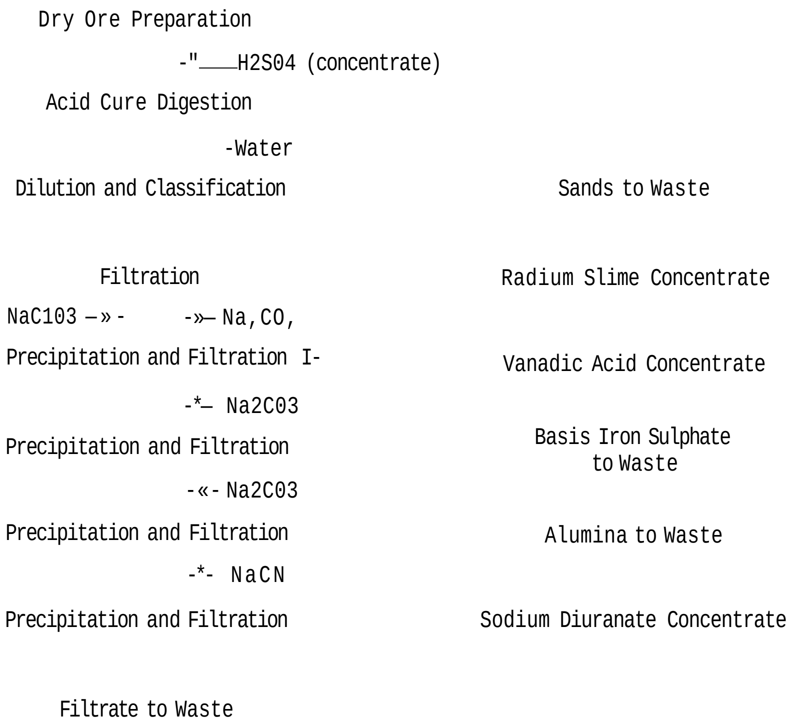


Figure 10 — North Continent Mines Company (Circuit 2)

except that the vanadium was precipitated as a sodium hexavanadate red cake rather than as an iron vanadate. The initial flowsheet is shown in Figure 12.

The ore was crushed and dry-ground to about minus-14 mesh and subsequently roasted with about 7 to 8 percent by weight of salt (NaCl). The roasted calcines were percolation leached with water, and the leached residue was sluiced to a tailings pond. The vanadium values were recovered from the pregnant liquor by the sodium hexavanadate precipitation procedure. Sulfuric acid was added, and the solutions were heated. After

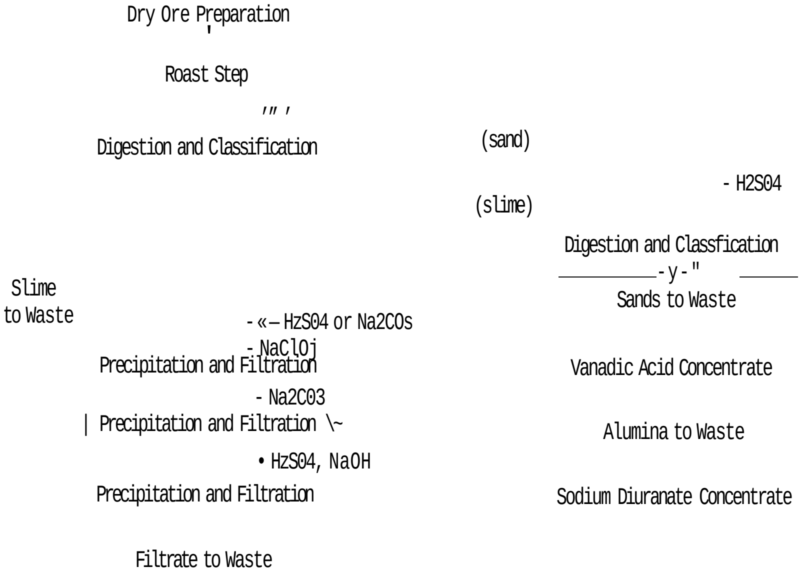


Figure 11 — North Continent Mines Company (Circuit 3)

several hours of heating and gentle agitation, the precipitation was complete, and the vanadium was concentrated into small spheroidal red-cake particles. This material was filtered, washed, and fused to form a product suitable for the manufacture of ferrovanadium. The fused oxide was shipped to Niagara Falls, New York, and other eastern plants of the parent corporation for the ferrovanadium conversion.

The operations of the Standard Chemical Company at Uravan, Colorado, were purchased by the Union Carbide Corporation; in 1936 a salt-roasting flowsheet similar to the Rifle circuit was placed in operation. In 1939 an acid-leach step was added for the extraction of uranium and additional vanadium. The regular salt-roast tailings were treated in this circuit.[109] In 1946 a somewhat similar circuit was added to the Rifle operation.

The original salt-roast plant at Naturita, Colorado, built by the Rare Metals Company about 1930, was not operated until 1939 when the Vanadium Corporation of America purchased the plant and rebuilt it.[111] The plant site, three miles from the town site of Naturita, was chosen because it offered a good combination of ore, water, and coal supplies.

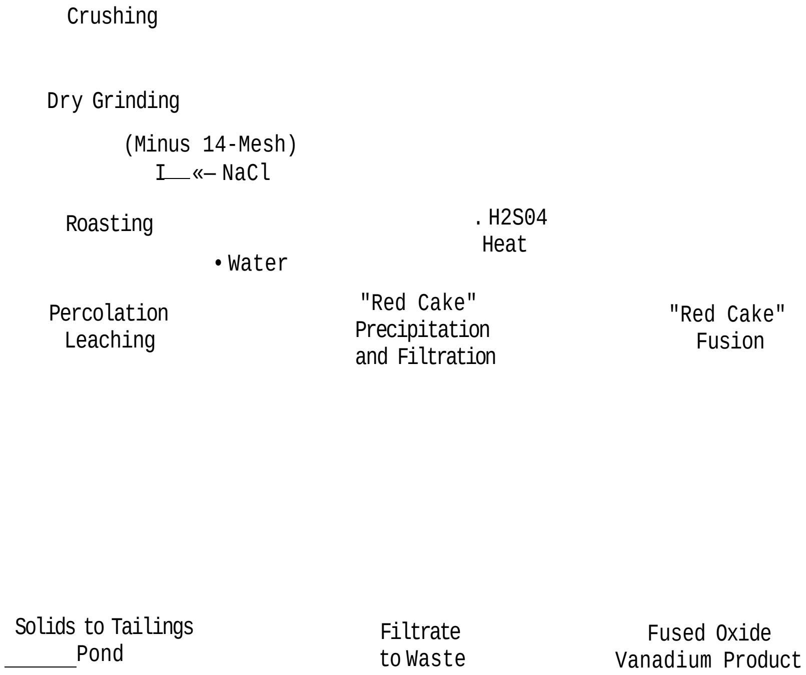


Figure 12 — Rifle Plant Flowsheet (About 1926)

The flowsheet, very similar to that of the Rifle mill (Figure 12), is described in detail by Kent.[111]

The ore was crushed to minus 1% inches in a jaw crusher, dried, and ground to minus-14 mesh in a rod mill. A six-percent-by-weight salt addition was made, and the ore was roasted in a multiple-hearth roaster. The terminal roasting temperature was approximately- 1600 °F. The hot calcines were quenched into water and leached in percolation tanks. A red cake was precipitated from the pregnant water-leach liquor by the addition of sulfuric acid and heat. As in the Rifle operation, enough acid was added to produce an acidity between 2.5 to 3.0 pH. The filtered and washed red-cake product was either dried or fused before shipment.

Developments During World War II

Two significant events took place during the early 1940's, one of which was to have a pronounced and prolonged effect upon the vanadium industry of Colorado. The first of these developments was the construction of two new vanadium mills located at Durango, Colorado, and Monticello, Utah, respectively. The war effort had increased the demand for vanadium, and in 1941 the U. S. Government financed the construction of these mills through its agent, the Metals Reserve Company. The second and most important event was the advent of the nuclear-energy program in 1942-1943 when the Army Corps of Engineers started recovering uranium from the Uravan tailings for the Manhattan Project. Within a relatively few years, uranium was destined to become the major product from the Colorado operations, and vanadium was again reduced to a by-product status.

The new salt-roast vanadium mills which were constructed at Durango and Monticello had flowsheets similar to the earlier Rifle and Naturita operations. The Durango mill was built and operated by the United States Vanadium Company. The plant site had formerly been occupied by a lead-zinc smelter which was converted to vanadium production within 66 days after construction was started in early 1942.n-

The Monticello mill was designed and operated by the Vanadium Corporation of America. The mill, a completely new plant, was placed on stream in August 1942. The flowsheet was a slight modification of the Naturita flowsheet. Pyrite was added to counteract the undesirable roasting effect produced by the "high" lime ores of the area; an alkaline-sodium carbonate leach solution was used in place of the neutral water-leach liquors that had been used in previous circuits. The Mining World Magazine 113 gives the following brief description of the Monticello flowsheet:

"The carnotite ore is mixed with iron pyrite (3 percent addition), crushed, dried to 3 percent moisture, ground to minus 10-mesh, mixed with ordinary salt, roasted, and leached with a soda ash solution. The vanadium is precipitated from the solution by addition of sulfuric acid, the precipitate is washed, partially dried, fused into a cake, and shipped for conversion to ferro-vanadium for use in making steel alloys." A moderately detailed process flowsheet and description are also presented in the article.

The Durango and Monticello operations were temporarily shut down in 1946.

Other salt-roast vanadium plants also operating during this period were the Gateway Alloys mill at Gateway, Colorado, (1941 to 1943) and the Blanding Mines Company mill at Blanding, Utah, (1940 to 1943).

By 1943 the Army Corps of Engineers was operating leaching plants for the recovery of uranium from the salt-roast tailings of the Uravan and Durango vanadium circuits. Uranium-vanadium concentrate produced at each of the plants was shipped to Grand Junction, Colorado, for additional refining. The refinery flowsheet (Figure 13) has been described by Lake and Lundquist.[109]

The salt-roast tailings were leached with about a 3 to 5-percent sulfuric acid solution in percolation leach tanks. The uranium and vanadium values which went into solution were recovered as a "green sludge." This sludge was precipitated by adding NaXOo or NaOH to the acid-leach liquors after the vanadium had been reduced to the quadrivalent state with metallic iron. The "sludge" was filtered, dried, and shipped to the Grand Junction refinery, which was located on the site of the present U. S. Atomic Energy Commission compound at Grand Junction; the operation was basically a soda-ash roast process. The dried sludge was mixed with sodium carbonate and roasted at about 750 °C in a Skinner multiple-hearth furnace. The vanadium was converted to sodium vanadate and was recovered from the calcines by water leaching. An alumina-cake precipitation step was used to decrease the phosphorous content of the water-leach liquors, and a red-cake product was then precipitated by the normal sulfuric acid procedure. The uranium remained in the water-leached residue, and this product was dried and shipped to eastern plants for additional purification.

Developments After 1946

During the postwar period between 1946 and 1948, all of the vanadium mills were shut down with the exception of the plants at Rifle and Naturita. In 1948 the U. S. Atomic Energy Commission inaugurated a new domestic uranium-production program which reactivated many of the older plants. With the new uranium ore processing plants constructed, 26 uranium and uranium-vanadium mills are now in operation; of these six are producing vanadium. Flowsheets for the four vanadium-producing plants located in Colorado are described on pages 102 to 119. The other two uranium-vanadium plants are the Mines Development Inc. mill at Edgemont, South Dakota, and the Kerr-McGee Oil Industries operation at Shiprock, New Mexico. Postwar developments in the extractive metallurgy of vanadium are described on pages 90 to 102.

RECENT PROCESSING DEVELOPMENTS

The extraction and recovery of vanadium from its ores is a good example of the practical and empirical processing technology preceding the theoretical understanding of the process chemistry. Even today many of the reactions which have been used for years in the processing operations are not quantified. The salt-roasting procedure has been practiced in Colorado since about 1910, but one of the few if not the onh known

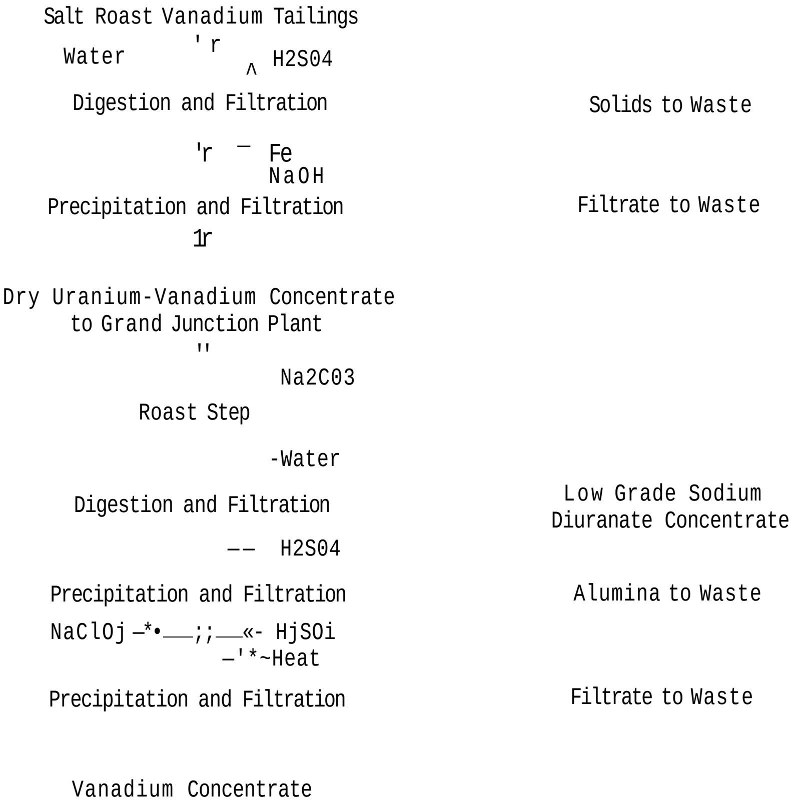


Figure 13 — Tailings Treatment Plant, Manhattan Project

discussion of the kinetics of this reaction was presented recently by Dresher.114 The ionization and reaction mechanism of the red-cake precipitation technique is not definite. Several theories on the ionization of vanadium in acidic solutions have been proposed, but the differences between the hypotheses apparently have not been resolved.

Virtually every article and publication on vanadium processing and vanadium chemistry comments on the complex and seemingly unpredictable behavior of vanadium in both acidic and alkaline solutions. Probably a significant percentage of the apparently erratic reactions observed and reported have been due to the unrecognized effects of other elements and complexes. The operators of vanadium producing mills have learned that almost trace amounts of other elements can have a pronounced effect upon the behavior of the milling circuits. Plants such as those operating in Colorado which process ores from many different mining operations find that a single new ore can introduce unexpected changes in process reactions. Problems and circuit bottlenecks which come and go often before a rational explanation can be developed have been an intrinsic part of vanadium recovery operations.

Previous sections of this report have shown that nearly all domestic vanadium production has been from the Colorado Plateau area. A substantial share of the balance of current world vanadium production is derived from the vanadium-bearing titaniferous magnetite iron ores being mined and processed in Finland and South Africa. The lead and zinc vanadates of Northern Rhodesia are also an important source of vanadium.

Vanadium is now being recovered as a byproduct from manufacturing elemental phosphorus; extracting vanadium from certain crude oils is also receiving some study.

The processing developments which have occurred during the past 10 to 15 years are discussed in the following paragraphs.

Processing Colorado Plateau Deposits

Colorado vanadium production has come from carnotite and roscoelite deposits, but during the past 10 years, essentially all production has been from the carnotite-type ores. Although uranium has been the major product during the period, vanadium processing has been affected by the extensive research and development programs on uranium recovery. The processing techniques or operations which have been adopted by the uranium-vanadium processing mills can be classified in the following three categories:

1. Extraction or solubilization of vanadium
2. Uranium-vanadium separations
3. Recovery of vanadium from solution and product purification.

Although these are not completely clean-cut distinctions, the classifications can serve as a basis for examining process developments.

Extraction or Solubilization of Vanadium

The salt-roast and acid-leach processes are currently being used to bring vanadium into solution. The basic steps being followed are quite similar to those of the earliest operations, but improved equipment and controls have increased processing efficiency. Flowsheets of current plant practice in Colorado are presented on pages 102 to 119.

Salt Roasting. The classical salt-roasting procedure consists of mixing the ground ore with salt and roasting the mixture for 60 to 90 minutes at about 850 °C. With proper roaster control, between 70 and 80 percent of the vanadium in the ore is converted to water-soluble compounds. This soluble vanadium is quickly taken into solution when the hot calcines drop into the quenching or cooling-leaching operations that follow the roasting step. After the soluble vanadium values are removed during the water-leaching operation, the uranium and some additional vanadium are recovered by acid leaching.

During the past 10 years the primary emphasis has been on uranium production, and the conditions of the roasting operation have often been a compromise between those that are optimum for uranium extraction and conditions that favor the vanadium conversion.

A number of different vanadium-bearing minerals are present in carnotite-type ores; thus a variety of complex reactions undoubtedly occur during the roast. Recently, however, Dresher has demonstrated the importance of two reactions which occur during the formation of water-soluble sodium-vanadate compounds by the salt-roast process.[114] Both reactions involve the oxidation of sodium chloride. In one reaction the oxidation is by water vapor and in the other by oxygen. The over-all reactions can be presented as follows:

$$2NaCl + V_2O_3 + H_2O \rightarrow Na_2O \cdot V_2O_5 + 2HCl \quad (1)$$

$$2NaCl + V_2O_5 + 1/2O_2 \rightarrow Na_2O \cdot V_2O_5 + Cl_2 \quad (2)$$

Dresher's findings show that the first reaction is the more predominant of the two. The rate-controlling step for this reaction is apparently the decomposition of a water-NaCl species at the gas-solid interface. The rate of oxidation of sodium chloride by oxygen is dependent upon the diffusional process which carries the oxygen from the gas-solid interface to the reactive site. Experimental studies and actual milling experience have indicated that a variety of operating variables must be considered to assure a successful salt-roasting conversion. These process variables include such things as ore constituents, grind, reagent additions, roasting temperature, roasting time, and roasting atmosphere.

The limestone or calcium carbonate content of the ore is one of the gangue constituents which can markedly affect the salt-roast reaction. Calcium compounds can react with the vanadium-bearing minerals to form calcium vanadates insoluble in water. Carnotite ores (at 1.5 percent V_2O_5) containing less than 3 percent $CaCO_3$ are the most desirable roaster feeds. If the lime ($CaCO_3$) content exceeds 6 percent, the formation of the calcium vanadate becomes excessive, and the water-leach extraction of vanadium drops below 60 percent. Some data and operating experience have indicated that ratio of $CaCO_3$ to V_2O_5 is also a variable. As the vanadium grade of the roaster feed increases, the permissible lime content of the ore can also increase. Some carnotite ore concentrates containing 4 percent or more V_2O_5 have been successfully roasted even though the $CaCO_3$ content was greater than 6 percent. Burwell[115] has stated that a variety of other calcium compounds can form during the roasting reactions and that the compositions depend upon the ratio of the constituents in the ore together with roasting conditions. Some of the reaction products mentioned include calcium silicate, calcium iron silicate, and complex calcium-iron-magnesium-aluminum silicates. The formation of the complex calcium iron silicates apparently represses the formation of the water-insoluble calcium vanadates, and iron pyrites have been used as a roaster-feed additive to promote this favorable equilibrium.[113] Pretreatment of "high lime" ores with sulfuric acid or sulfuric-hydrochloric acid combinations have been used. The objective of these preroast operations is either to convert the $CaCO_3$ to the less reactive $CaSO_4$ or to dissolve partially and remove the lime as soluble $CaCl_2$.

Other ore components — phosphorus, arsenic, and molybdenum — can principally affect the separation and precipitation of vanadium: whereas organic materials can produce an undesirable reducing atmosphere in the roaster. An efficient salt-roast conversion may be obtained by grinding the ore fine enough to give a reasonable degree of liberation. The vanadium values in the carnotite ores are associated with the cementing materials between the silica grains of the sandstone matrix. For most Colorado ores a minus-14-mesh grind will expose the vanadium minerals. Other vanadium-bearing ores such as the titaniferous magnetites must be ground much finer before efficient roasting reactions are possible. u«29 117 jf tne sajt an(j ore are we]j blenclec[before entering the roaster, a minus-10-mesh salt can be used: The salt-roast conversion is probably a solid-liquid-gas reaction; Dresher[114] has shown that the reaction rate nearly doubles when the roasting temperature reaches the melting point of sodium chloride (800°C). If the reaction mechanism was not dependent upon the uniform reagent distribution provided by the molten NaCL, a finely pulverized salt would probably be necessary.

The standard rule of thumb for salt additions to roast operation has called for an addition of 6 percent salt plus an additional 1 percent of salt for every percent of vanadium present in the ore. Experimental and operating experience has shown that for optimum extractions, the residual NaCl content of the roaster calcines should be about 1 to 2 percent. If the residual NaCl is less, the vanadium extractions can usually be improved by increasing the salt addition. Other roasting reagents such as sodium carbonate and sodium sulfate have been used. The principal application of sodium carbonate has been for roasting vanadium-bearing precipitates and other high-grade or low silica materials. Sodium chloride is a more selective and desirable roasting reagent for silicious ores. Sodium carbonate reacts with silica to form soluble sodium silicate compounds which complicate subsequent separations and precipitations. Sodium sulfate is also an effective roasting reagent, but economic considerations have favored the use of sodium chloride in the Colorado Plateau operations.

The roasting time and temperature are important process variables. The optimum conditions for individual ores do vary, but most carnotite-type ores respond to roasting temperatures between 820° and 850 °C. The permissible temperature variation is often small, and temperature control within a plus or minus 5 °C range would be very desirable. At temperatures much above 850 °C, the vanadium extraction usually decreases. The exact mechanism of this loss, referred to as the "silica tie up," has not been identified; but a silica-vanadium association is indicated because much of the vanadium can be recovered during laboratory tests by leaching with dilute hydrofluoric acid. Equivalent strengths of sulfuric or hydrochloric acid do not extract this vanadium.

In general, the higher roasting temperatures also adversely affect the uranium extractions which can be obtained during the acid-leaching operation on the roaster calcine. Although the uranium minerals are not converted to water-soluble compounds during the salt roast, the composition of the uranium-bearing compounds is altered. Probably some form of sodium or potassium uranate is produced. Evidence of a change is indicated by the greatly increased acid-leach extraction rates of the uranium in salt-roasted calcines over that obtained on the same ore before roasting.

The optimum retention time at roasting temperature is normally between 60 to 90 minutes. The initial reaction rates of the salt-roast reaction are relatively fast: Dresher's data 114 show that at least one of the major reactions is approximately first order. Probably over 70 percent of total conversion is completed within the first 20 minutes at roasting temperature, but because the reaction is concentration dependent, the rate decreases quite rapidly.

The reduced extractions associated with either excessive roasting time or temperature are also referred to as loss caused by "over roasting." The sensitivity of ores to over roasting varies, but in general the oxidized ores are somewhat less sensitive than the more reduced ores in which at least part of the uranium and vanadium are in the lower-valence states.

The vanadium must be in the pentavalent state before the salt-roasting reaction can occur. If the ore feed contains minerals in which the vanadium is present in the trivalent or quadrivalent state, the minerals must be oxidized before water-soluble vanadium can form. Good roast conversions are assured by maintaining an oxidizing atmosphere in the roaster. If reducing environment is present within the roaster, the pentavalent vanadium will be reduced, and the production of water-soluble vanadium compounds will be very low. Probably the principal cause of reducing atmospheres during salt roasting is the presence of organic material in the ore feed. Even these materials can be roasted, however, if sufficient contact and retention time are allowed for essentially complete oxidation before roasting temperatures are reached.

Acid Leaching. The acid-leach recovery of vanadium was practiced in a number of early Colorado mills, but most of the vanadium production in Colorado has been from salt-roasting operations. During the past year several U. S. plants have started producing vanadium via an acid-leaching route. This revival of vanadium recovery by acid leaching has been a byproduct of the developments on acid-leach recovery procedures for uranium. Most of the uranium-recovery operations are based on acid-leach circuits, and some of the ores contain appreciable amounts of vanadium.

In general, the vanadium content of the Colorado Plateau ores is more refractory to acid leaching than is the uranium fraction. A relatively mild acid leach which will dissolve 90 to 95 percent of the uranium values will solubilize only 30 to 35 percent of the vanadium in the ore. Much of the vanadium content of the carnotite ores is associated with clay minerals which are not readily attacked by acid solutions. However, the possibility of increasing vanadium extraction in the acid-leaching circuits has been of interest to the uranium industry. The vanadium is brought into solution by increasing the acidic strength of the leaching liquors by raising leaching temperature and, in some cases, by adopting longer extraction times. If severe enough conditions are used, essentially complete acid-leach recoveries of vanadium are technically feasible, but economic factors such as reagent costs and capital investment limit the practical recoveries that can be realized for any given ore supply.

Another factor which has helped to revive the interest in acid recovery of vanadium is the development of ion exchange and solvent-extraction techniques that can separate uranium and vanadium in acidic solutions. Similar procedures have also been developed that can recover vanadium from acid solutions. Four uranium-vanadium mills are using solvent-extraction techniques for the recovery of vanadium.

Uranium-Vanadium Separations

Separation of uranium and vanadium has been one of the principal problems of the Colorado vanadium industry. Until the installation of the first uranium ion-exchange plants in the early 1950's and the construction of the initial solvent-extraction circuits in about 1957, the uranium-vanadium separations had been based either on roasting and fusion reactions or on rather touchy chemical-precipitation operations.

The salt-roasting procedure has provided an economical technique for bulk separation of vanadium from uranium, undoubtedly one of the reasons why this procedure has remained in use for many years. The chemical separation of uranium and vanadium in acidic solutions is difficult and relatively expensive. The flowsheets given in pages 75 to 90 describe some of the procedures that have been used.

Both the ion-exchange and solvent-extraction separation for uranium and vanadium were developed by research programs sponsored by the U. S. Atomic Energy Commission and its predecessors. Many of the government reports that have been published on both the ion-exchange and solvent-extractions procedures are cataloged in the Nuclear Science Abstracts.

The ion-exchange and solvent-extraction separations are based on the ability of the organic compounds of the amine and organophosphorous families to exchange uranium ions selectively from solution.

The ion-exchange resins used in the uranium industry are classified as anionic resins. The active exchange site is a quarternary amine structure capable of selectively exchanging the uranyl sulfate anionic complex away from quadrivalent vanadium cations. The amine reagents used for the solvent-extraction procedures are liquid anionic ion-exchange reagents which function similarly to the solid ion-exchange resins.

The organophosphoric acid solvent-extraction reagents are cationic exchangers. The uranyl cations exchange with the hydrogen of the organophosphoric acid.

The uranium ions held on the exchange sites of the resins or solvent-extraction reagents are eluted or stripped from the reagent with solutions of various inorganic compounds. Acidified chloride, nitrate, and sulfate solutions are used to elute or strip uranium from the ion exchange resins and the amine-type liquid-ion-exchange reagents. Sodium carbonate is used to strip the uranium values from the organophosphoric acid-extraction reagent.

A description of the function and application of ion exchange and solvent extraction in several current uranium-vanadium flowsheets is given on pages 102 to 119.

Recovery of Vanadium from Solution and Product Purification

The uranium-free solutions produced by the salt-roast operations are slightly basic; whereas the uranium-barren effluent or raffinate from the ion-exchange and solvent-extraction separations is acidic. The procedures used for recovering vanadium from the acid liquors are more complex than those used to recover vanadium from neutral or basic solutions.

Recovery of Vanadium from Acidic Solutions. The solvent-extraction or liquid-ion-exchange techniques for recovering vanadium from acidic solutions have probably been among the most significant developments in vanadium processing during the last 10 years. This improvement was an ancillary result of investigations on uranium recovery. In general, under proper conditions the reagents used for uranium extraction can be made to function as ion-exchange agents for vanadium. Much of the early work on the solvent extraction of vanadium was carried out at the Oak

Ridge National Laboratories between 1953 and 1955. The results of this work have been published by the Atomic Energy Commission in progress and topical reports. Some of the most significant data on vanadium extraction have been presented in ORNL 1903,ns ORNL 1964,110 ORNL 1970,120 and ORNL 2820.121

Although the organophosphorous and the amine-type reagents can be used for vanadium extraction, the Di-2-ethyl hexylphosphoric acid (DEPHA) reagent now is the most widely used.

The current practice of vanadium-solvent extraction with DEHPA involves first adjusting the pH of the uranium-barren liquors to about 2.0 and determining that the iron is in the ferrous state. The adjusted solutions are then extracted with an organic liquid containing approximately 15 parts DEHPA and 85 parts kerosene or similar diluent. Usually four or five stages of countercurrent extraction are used. The "loaded" solvent is stripped with a 5 to 15-percent H2S04 solution, and the stripped solvent is recycled to the extraction or loading circuit. Because the acid strip does not remove all of the elements which can be exchanged by the solvent, part of the recirculating solvent is stripped with a sodium carbonate solution. This "clean up" treatment completely regenerates the reagent and prevents loss of loading efficiency. The product or strip liquor is an acidic solution of quadrivalent vanadium ions which usually also contains some iron and phosphorus. A description of several vanadium solvent-extraction operations is presented on pages 102 to 119.

Experiments have shown that the amine-type liquid-ion-exchange reagents can be used in acidic and basic solutions.1-- 12" As mentioned previously, these reagents are anionic exchangers; therefore, the vanadium must be in the pentavalent state before the exchange can occur. Several plants are either using or considering using the amine-type reagents for vanadium extraction.

Vanadium is also being recovered from uranium-barren acid solutions by a combination of precipitation and roasting procedures. The solutions are precipitated, and the vanadium-bearing solid that is recovered is roasted with sodium carbonate. The vanadium is converted to sodium metavanadate which is subsequently recovered into an alkaline-leach liquor. A standard red-cake product is precipitated from this solution.

Recovery of Vanadium from Neutral or Basic Solutions. The vanadium bearing solutions from the salt-roast operations are either neutral or slightly basic. The red-cake precipitation technique is used to recover the vanadium from these solutions; the over-all reaction can be represented as follows:-"

6NaVO:1 + 2H2S04 -> Na2H2V,;017 +2Na2 S04
Sodium Sodium
Metavanadate Hexavanadate

This simplified equation does not indicate the complexity of reactions that occur. The solution chemistry of pentavalent vanadium in acidic solutions is probably one of the least defined facts of inorganic chemistry. Nevertheless, this reaction has been the basis for vanadium recovery from water-leach liquors for many years, and the precipitation procedure has developed as an art.

Many modifications of the procedure have been practiced, but in general the technique involves adding sulfuric acid to a water leach vanadium liquor containing about 15 g/1 of V20r, and heating this solution to about 80° to 90° C. The optimum pH for precipitation is usually between 2.5 to 3.0; "Congo Red" indicator paper has been used for many years to indicate the proper acidity for the reaction. The precipitation is usually made in wooden tanks fitted with slow-speed sweep agitators. The precipitation rate is relatively slow: from 1 to 6 hours are often needed to complete the precipitation. In many ways the red-cake formation appears to resemble a polymerization reaction. Some of the variables which apparently can influence the precipitation include the following:

1. Vanadium grade of the feed solution
2. Method of adding the sulfuric acid
3. The heating method and rate
4. The precipitation temperature
5. The size of the tank
6. The type, position, and speed of the agitation
7. The presence of "seed particles" of red-cake from previous batches

The red-cake precipitate is a sodium hexavanadate salt; the color of the small spherical particles which form ranges from an orange-red tone to a brown-red shade. The theoretical vanadium content of sodium hexavanadate is equivalent to 87.2 percent V20.-,, and the commercial red-cake products produced by the above procedure contain 83 to 86 percent V20-,. The filterability of a properly precipitated red-cake is very good.

Recent studies have shown that quaternary ammonium chloride compounds can be used to solvent extract vanadium from neutral or alkaline solutions. Several different types of stripping solutions can be used, and the production of high-purity vanadium compounds directly from these strip liquors is technically feasible.

Purification of Vanadium Compounds. Before about 1958, the 88 to 92-percent-V20-, "fused oxide" product produced directly from red-cake was the standard commercial item. During the past two or three years. several producers have marketed plus-98-percent-V20,-, fused-oxide products. Details of production methods for these high-grade materials have not been published, but in general the procedures involve either:

1. The decomposition and fusion of ammonium metavanadate or ammonium poly-vanadate compounds produced by redissolving red-cake and making a second precipitation; or

2. the partial precipitation of the product liquors from vanadium-extraction circuits using the DEHPA reagent; or

3. the precipitation of the strip solutions from amine-solvent-extraction operations.

The rapid pace of process developments in the uranium industry during the past 10 years has affected the vanadium industry of Colorado. The uranium and vanadium mills were the first metallurgical industries able to apply ion-exchange and solvent extraction separations. These industries have also fostered the development and improvement of acid-resistant processing equipment. The procedures and equipment developed for the uranium and vanadium flowsheets will undoubtedly be applied in other segments of the metallurgical industries.

Recovery from Iron Ores

The vanadium-bearing titaniferous magnetite ores, one of the largest potential sources of vanadium, are being processed for vanadium recovery at an operation in Finland (Otanmaki) and at Witbank, South Africa.

The primary purpose of the Otanmaki operation was to produce an iron-ore concentrate. Mineral-dressing techniques were used to separate the ore into magnetite and ilmenite fractions. Most of the vanadium is carried with the magnetite concentrate, and the vanadium content of this material is equivalent to about 1 percent V20-,.

The plant started vanadium production in June 1956.1-;! The initial production rate was approximately 1,000,000 pounds of V20-, per year: the present annual output is about 2,000,000 pounds of V20.-,.113

The magnetite concentrate is dried, mixed with sodium sulfate, and the mixture is finely ground in a dry-grinding circuit. The mixture is then pelletized to form about 1-inch-diameter balls which are fed to a vertical-shaft furnace. This furnace, apparently a modification of the units used to sinter iron-ore pellets, is specially designed to provide the proper conditions for the roasting reaction. The roasting temperature is about1200°C.

The pelletized calcine is leached with hot water, and after washing, the pellets are marketed as a high-grade iron-ore sinter. The pregnant water-leach liquors contain over 25 grams per liter of V20-„ and a red-cake is precipitated by adding sulfuric acid. Although Merenmies1"' has indicated that the initial vanadium is purified before fusion, he has not specified the procedure. The final product has an analysis of 90 to 92 percent V2O0 and about 2.0 percent Na20.

At Witbank, South Africa, the Minerals Engineering Company is recovering vanadium from selected high-grade titaniferous magnetite ores 115 having a vanadium content of about 1.5 percent V_2O_3. The vanadium values are recovered by the salt-roast process. Multiple-hearth roasters are used at this plant, and the roaster feed is a mixture of minus-60-mesh ore and salt. The salt addition is equivalent to about 8 to 10 percent of the ore weight. The roasting temperature, maintained for about one hour, is 800 °C.

The vanadium is leached from the calcines with water and later precipitated as ammonium metavanadate by adding ammonium chloride. This product is decomposed and fused to form a very high-grade fused-oxide material. A unique feature of the Witbank operation is the recovery of NH_4C1 and NaCl from the waste liquors of the vanadium-precipitation operations. This procedure was adopted because fuel is relatively cheap in the area and reagent costs are high. The NaCl and NH_4CI, recovered by evaporation and crystallization, are reused in the roasting and precipitation operations.

During emergencies created by war vanadium has been recovered from slags formed during the smelting of vanadium-bearing iron ores. Most of the vanadium collects in the molten pig iron, and when this material is blown in an acid converter, the vanadium is transferred to the slag. This slag is then cooled, crushed, and salt roasted. Nearly all of the German and Swedish vanadium production during World War II was obtained by this method.

In the U.S. a considerable amount of experimental work has been done on the recovery of vanadium from domestic deposits of the titaniferous magnetites. The deposits are not being worked for vanadium recovery, although magnetite and ilmenite concentrates are being produced at the Tahawas, New York, operations of the National Lead Company. The U. S. Bureau of Mines has published several reports on various process development studies.

Recovery of Vanadium from Other Sources

Between 1941 and 1954 the Anaconda Company produced about 150 tons per year of V_2O_5 from its phosphoric acid and phosphate-fertilizer operations in Idaho. An impure phosphato vanadic acid was precipitated from the phosphoric acid solutions, and the vanadium in this product was separated from the alumina, iron, and phosphate contaminants by several stages of purification. Part of the phosphate was removed by treating the precipitate with sodium carbonate and calcium chloride. The phosphate precipitated as calcium phosphate and the vanadium remained in solution as sodium vanadate. The phosphate remaining in solution was removed by a carefully controlled lime treatment which precipitated the phosphate as dicalcium phosphate. A standard sodium hexavanadate red cake was then precipitated by the addition of sulfuric acid.

In recent years a new source of vanadium has developed as a byproduct of the Western elemental-phosphorus industry. The western phosphate ores, containing from 0.1 to 1.0 percent V20,-„ are reduced to elemental phosphorus in an electric furnace to produce a slag containing an equivalent of 7 to 10 percent V20-,. The Minerals Engineering Company is processing these phosphide slags for vanadium recovery at a new plant near Salt Lake City, Utah. Although details of the processing technique have not been published, it is understood that the flowsheet consists of a modified salt roast followed by solvent extraction of the subsequent leach liquors.

Since 1930, vanadium has been produced as a byproduct from the lead-zinc operations at Broken Hill in Northern Rhodesia. The vanadium which occurs as descloizite and vanadinite is concentrated by gravity and flotation methods.87 124 At least part of the product is purified by chemical processing, and both physical concentrates and chemically refined products have been shipped.

The vanadium deposits at Minas Ragra, Peru, produced a significant percentage of the total world vanadium supply. Most of the vanadium production from this mine, discovered in 1905 and operated till 1955, was derived from vanadium sulfides and vanadium-bearing organic materials. The ores were salt roasted, and a type of red-cake was precipitated from the leach liquors.

The possibility of recovering appreciable amounts of vanadium during refining some crude oils has been considered.

CURRENT DOMESTIC VANADIUM PRODUCTION FLOWSHEETS

Vanadium is being extracted from domestic U. S. ores at seven milling operations:

Colorado Mills

(1) Climax LIranium Company	Grand Junction, Colorado
I 2) Union Carbide Nuclear Company	Rifle, Colorado
(3) Union Carbide Nuclear Company	Uravan, Colorado
(4) Vanadium Corporation of America	Durango, Colorado

Other Mills

(5) Kerr-McGee Oil Industries	Shiprock, New Mexico
(61 Minerals Engineering Company	Salt Lake City, Utah
(7 I Mines Development Company	Edgemont, South Dakota

Process descriptions and flowsheets for the current Colorado vanadium producing mills are presented in the following paragraphs together with brief descriptions of the operations in other states.

Vanadium processing in Colorado is a blend of milling and chemical production procedures and problems. Many of the current techniques are similar to those of the heavy chemical industries; whereas the materials-handling problems and variable feed materials are more characteristic of milling operations on other ores. Each step of the process is dependent upon the feed material; if the ore changes, the process must be modified to accommodate this change. Hence the philosophy of plant operation and the actual physical arrangement must remain quite flexible. Optimizing a given facet of the operation is more difficult than doing an equivalent job in a chemical plant where the feed materials are relatively uniform.

In some industries, the reagent costs are a major item, whereas in others, labor costs are more significant. In the Colorado vanadium industry, the ore costs are a significant portion of the total, but on the basis of the available information it is difficult to single out any other specific expense item. For evaluating the desirability of a process change, all cost factors including capital, labor, and reagents must be considered, along with the benefits of increased recovery or product purity.

Colorado Mills

The four Colorado vanadium-producing mills account for approximately 80 percent of the current domestic vanadium output. The flowsheets of these mills represent a cross section of modern vanadium-production technology. The classical techniques of salt roasting and chemical separations together with some of the most recent developments in acid leaching and solvent extraction are practiced in these mills.

The descriptions of the individual mill flowsheets are as follows:

PROCESS DESCRIPTION AND FLOWSHEET

(Aug. 11, 1961)

Climax Mill

Operator:	Climax Uranium Company Unit of American Metal Climax, Inc.
Location:	Grand Junction, Colorado
Rated Plant Capacity:	330 TPD
Products:	Fused Vanadium Oxide Yellow-Cake Uranium Product
Process:	Extraction: Salt Roast-Water Leach Acid Leach Uranium-Vanadium Separation: Solvent Extraction on Acid Liquors Vanadium Recovery: 1. Red-cake precipitation and fusion

The current salt-roast acid-leach solvent-extraction process now in use at the Climax Uranium Company plant was adopted in 1956. Before

1956, the uranium-vanadium separation on the acid-leach liquors was based on a uranyl phosphate precipitation technique.

The salt-roasting flowsheet is a modification of the classical salt roasting practice. Only the slime fraction of the ore, however, passes through the roasters. A sand-slime separation is made on the ore pulp, and the uranium and vanadium values are recovered from the sand fraction by acid leaching. These acid-leach liquors are precipitated by neutralization in a two-stage conditioning circuit, and the precipitate is combined with the slime fraction of the ore and fed to salt-roast operation.

The calcines after roasting are water leached to dissolve the vanadium that is converted to sodium vanadate by the roasting reaction. The conditioning and desliming circuits serve to interlock the salt roast and acid-leach operations, and all recovered vanadium is obtained via the water-leaching operation. A vanadium red-cake, precipitated from these water-leach liquors, is then fused and flaked.

The water-leach calcines are acid leached, and the uranium is recovered from the acid-leach liquors by solvent extraction. The vanadium values in the solvent-extraction raffinate are precipitated in the conditioning circuit and recirculated to the salt roast.

A schematic flowsheet of the process is shown in Figure 14. (See fold-out sheet.)

Receiving, Crushing, Sampling, and Grinding

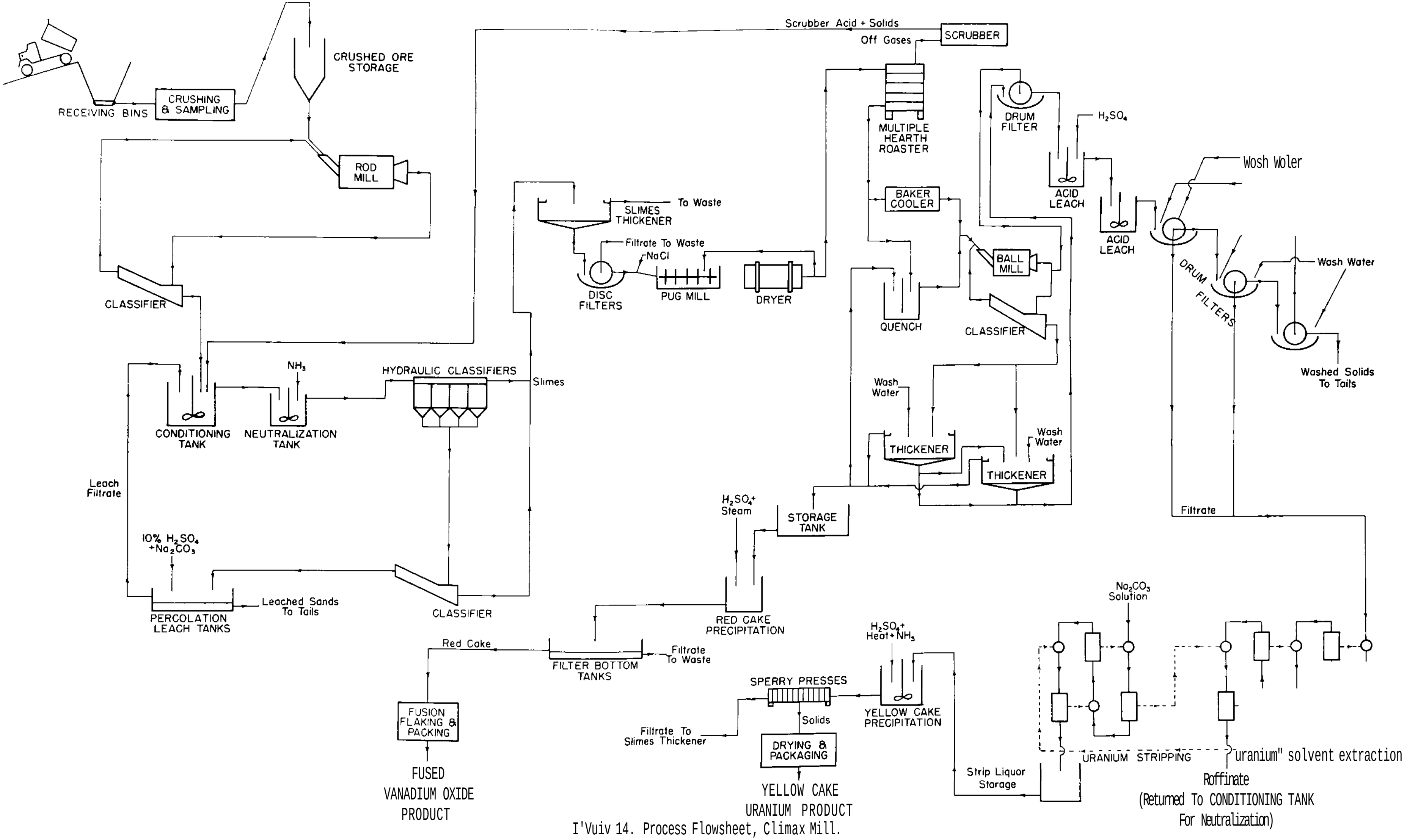
The run of mine ore received at the Climax Mill is reduced to a nominal minus-lV^-inch size in the primary crusher. This material is fed to the three-stage sampling plant. The crushed-ore and sample-plant rejects are stored in bins.

The minus-1'/'-inch ore is fed to a wet-rod mill circuit that produces a nominal 14-mesh-size product. The rod-mill circuit is closed with a classifier.

Conditioning and Desliming

The conditioning-desliming circuit has at least a six-fold integrated objective:

1. To deslime the rod-mill product and route only the slime fraction to the roast, thereby reducing the tonnage to the one available roaster and effectively increasing overall plant capacity.
2. To recover the uranium and vanadium values from the sand-leach operation and concentrate these values into a precipitate which will report with the original ore-slime fraction to the salt roast.
3. To recover and recirculate the vanadium values in the solvent-extraction raffinate to the salt roast.
4. To recover the uranium and vanadium values collected during the scrubbing of the roaster off gases.



I'Vuiv 14. Process Flowsheet, Climax Mill.

Climax I ranium Cu. (Aug. 11, 1961)

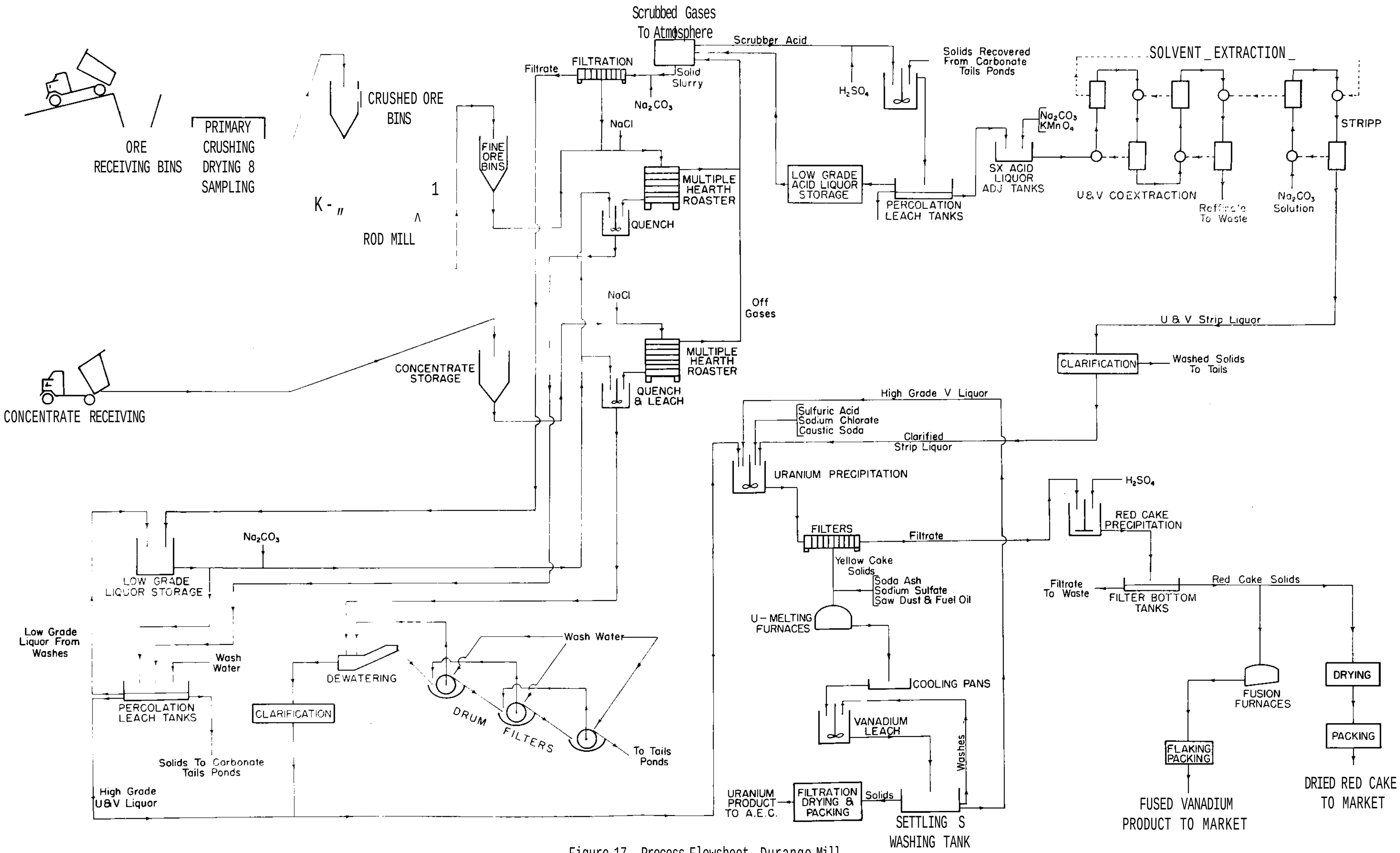


Figure 17. Process Flowsheet. Durango Mill.
Vanadium Corporation of America (Aug. 11, 1961).

5. To use the acid consuming characteristics of the ore as part of the neutralization requirements for the various acid streams that are neutralized in the conditioning circuit.

6. To convert the calcium carbonate in the ore to calcium sulphate.

The minus-14-mesh rod-mill product enters the first stage of the conditioning section where it is mixed with the acidic liquor from the sand leach, the roaster scrubber acid, and the raffinate from the uranium-solvent-extraction circuit. This acidity is partially neutralized by the ore. and the effluent from the primary conditioning operation has an approximate pH of 1.5 to 2.0. The neutralization and precipitation is completed by adding ammonia in the second conditioning stage. The final conditioning effluent has a pH of 6.5 to 7.

The finely divided precipitated values and the slimes are separated from the sand fraction on hydraulic classifiers at about 200-mesh size. The slimes are thickened and subsequently filtered on disc-type filters. The barren thickener overflow and filtrate are sent to waste. The plus-200-mesh sand fraction is pumped to percolation leach tanks.

Sands Leaching

After the sands are bedded into the percolation tanks, a hot 10 percent HaSOj leaching solution is down percolated through the bed. Sodium chlorate is used to increase vanadium recovery.

The acidic liquor from the leaching and washing operations is recirculated to the conditioning circuit, and the solids residue is pumped to the tailings ponds.

Salt Roast-Water Leach

The salt-roast operation at the Climax Mill is made on a pelletized feed. The slimes filter cake from the disc filters is pugged with NaCl and fed to a rotary dryer. The salt addition is equivalent to approximately 13 percent of the dry weight of the slimes. Part of the dryer discharge is recirculated to the pug mill. The recirculation helps to agglomerate the slimes, and the dryer product is a pelletized material with a :'x-inch average particle size.

The pelletized feed retains its form through the roasting operation. and after the pellets are cooled or quenched they are ground to about minus-65-mesh in a ball mill. Both a Baker cooler and a wet-quench system are used to cool the calcines which discharge from the roaster at about 800 °C.

The leached calcines are washed in a combination thickener-filter circuit, and the vanadium-pregnant water-leach liquor is pumped to red-cake precipitation.

Calcine Acid Leach

The washed water-leach calcine is acid leached for uranium recovery and some additional vanadium extraction. The circuit might be classed as a high density hot acid leach flowsheet.

The water-leach calcine filter cake with a minimum of dilution liquor, is fed to the agitation leach tanks and concentrated sulfuric acid is added. The pulp density in these agitators is at least 60 percent solids. The heat of dilution of the sulfuric acid that is added maintains an above ambient leaching temperature. The acid-leached calcines are washed in a three-stage drum-filter circuit. The filtrate which contains the acid-soluble uranium and vanadium is pumped to the solvent-extraction circuit.

Uranium Solvent Extraction

The uranium is separated from the vanadium in the acid-leach liquors by a solvent extraction with di-2-ethylhexyl phosphoric acid. Five loading stages are used, and the uranium is stripped from the loaded solvent with a 10 percent sodium carbonate solution in a three-stage circuit.

The uranium is precipitated from the loaded carbonate liquor by a two-stage procedure. First the carbonate is neutralized or "destroyed" by adding sulfuric acid and heating the liquor. The terminal acidity is in the 3.0 to 3.5 pH range. A sodium uranate yellow cake is then precipitated by the addition of ammonia. If the carbonate ions are not completely destroyed during the acidification, the yellow-cake precipitation with ammonia will not be complete.

The yellow cake is filtered, washed and dried. The filtrate and washes are recycled to the slimes thickener to recover any uranium solids that may inadvertently pass through the filter media.

The uranium-barren raffinate from the solvent-extraction operation contains the vanadium that was taken into solution during the acid leach of the roaster calcines. This solution is recycled to the conditioning-desliming circuit where the vanadium is precipitated and concentrated into the salt-roast feed.

Vanadium Precipitation

A sodium hexavanadate red cake is precipitated from the water-leach liquors by the standard technique. Sulfuric acid is added to maintain a pH of 3.0 and the solution temperature is held above 80 °C. The granular red cake that forms is filtered and washed on filter-bottom tanks. The washed red cake is fused, and as the molten oxide flows from the furnace, it is flaked on a chilled casting drum. The fused oxide product of approximately 88 percent V20-, is packed into steel drums for shipment.

PROCESS DESCRIPTION AND FLOWSHEET

(Sept. 8, 1961)

Operator: Union Carbide Nuclear Company
Location: Uravan, Colorado
Rated Plant Capacity : 1000 tons per day
Products:
1. Fused Vanadium (plus 98 percent V.O.-,)
2. Uranium yellow cake

Process: Extraction: Hot-Acid Leach
Uranium-Vanadium Separation: Column Ion Exchange
Vanadium Recovery:
1. "Ferric Vanadate" precipitation on Ion exchange uranium-barren liquor
2. Alkaline roast or leach of the ferric vanadate
3. Red-cake precipitation of liquors from roasting circuit
4. Purification of red cake and fusion of the product

The Uravan plant, located 90 miles southwest of Grand Junction. Colorado, is the only Colorado vanadium mill currently operating which does not use the salt-roast process. A "hot-acid leaching" treatment is used to extract the vanadium from the carnotite-type sandstone ores being processed at this plant. Both uranium and vanadium are taken into solution during the leaching operation, and a subsequent column ion exchange procedure is used to make a separation of these two elements.

The uranium is loaded on to the resin, and the vanadium passes on through the columns. The uranium is eluted from the resin with an acidified brine and processed to produce a yellow-cake uranium product which is sold to the Atomic Energy Commission.

The vanadium is recovered from the uranium-barren ion exchange effluent by a series of operations which include a "ferric vanadate" precipitation followed by alkaline roasting or leaching and precipitation of a red-cake vanadium product. The red cake is redissolved, purified by a second precipitation, and fused to produce the standard commercial vanadium "fused oxide" product. The Uravan "fused oxide" can be classed as a high-grade (+98 percent VoO,-,), low alkali product.

A schematic process flowsheet of the Uravan operation is shown in Figure 15.

Receiving, Sampling, Crushing, and Grinding

The Uravan plant receives ore from over 100 mining operations; the receiving and sampling sections are designed to handle a wide variet> of truckload and lot sizes. The run of mine ore is crushed to a minus-2-inch size and sampled. A three-stage bucket-chain sample system is used with intermediate crushing after the primary, secondary, and tertiar) sampling operations. The sampling procedures for uranium-bearing ores are specified by AEC contract regulations, and as with all other uranium processing mills, the sample plant is designed to meet these requirements.

The minus-2-inch ore which leaves the sampling plant is stored in bins and subsequently ground to a nominal minus-14-mesh product in two Aerofall Mills. These mills are autogenous dry-grinding units in which the finished product is removed from the mill by a controlled draft system. The finished product which is recovered from the air stream by an air-classification system is stored in bins and then fed to the leaching circuit.

Leaching

The dual purpose of the leaching circuit is to extract the uranium and vanadium values from the ore and to provide a pregnant solution with an acid concentration suitable for the subsequent ion-exchange separations.

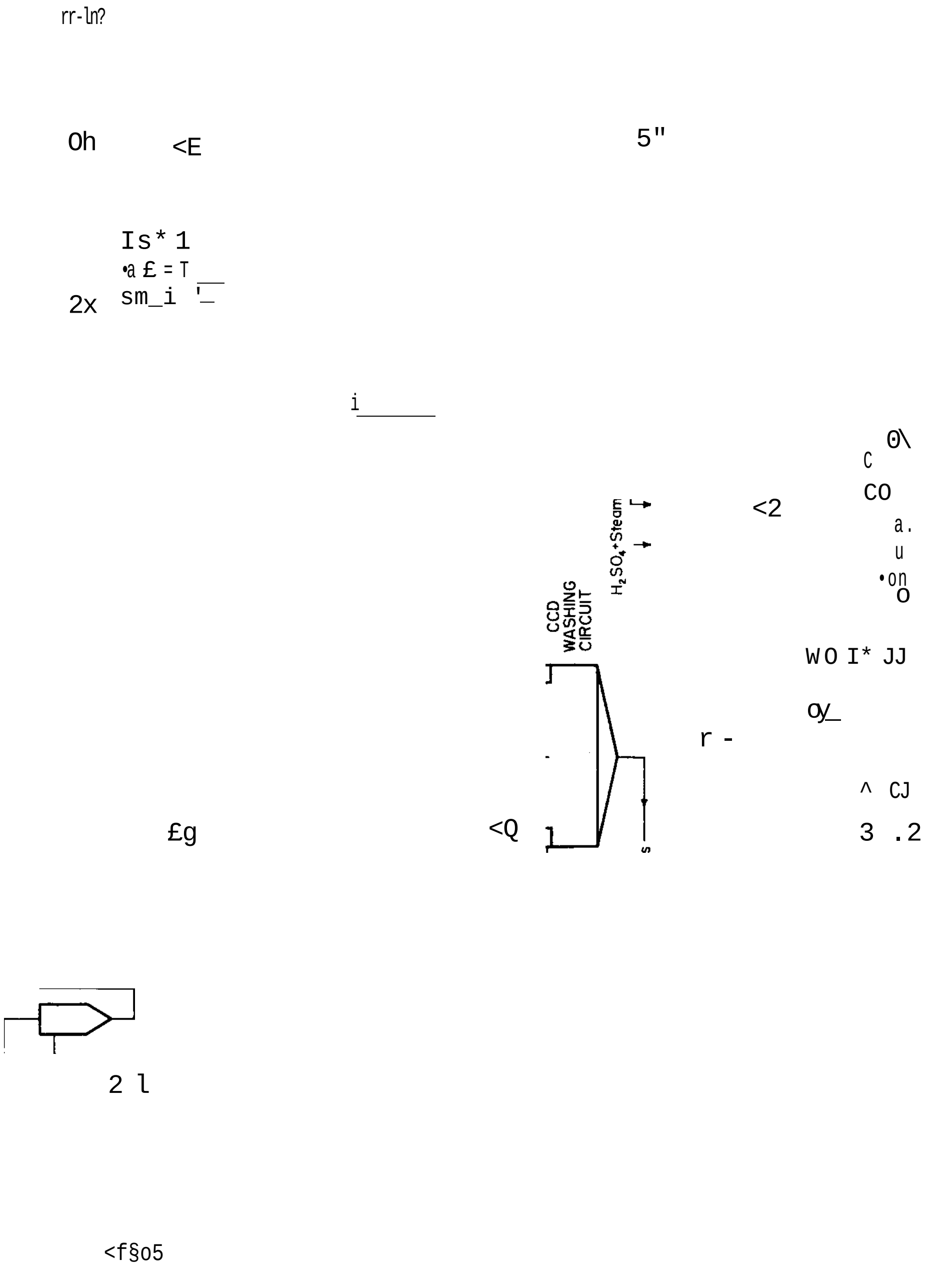
The process used is a modification of the two-stage leaching principle in which the pregnant solution is taken from the first stage. Leach liquors from the strongly acidic secondary stage are contacted with unleached ore in the primary digestion stage. The alkaline constituents of the ore react with the strongly acidic secondary digestion liquors, and a liquor which approaches the 1.5 pH acidity required for efficient ion exchange is produced. If the alkaline content of the ore is not sufficient to achieve the required neutralization, a second "acidity adjustment' is made with high-lime ores or limestone.

Steam and submerged combustion heating are used to heat the pulp to increase vanadium extraction. Substantial uranium extractions are possible at ambient temperatures, but some of the vanadium minerals are more refractory; consequently increased time, acidity, and temperature are necessary to raise the vanadium extraction above 40 percent. The leaching-circuit temperatures are maintained in the proximity of 80°C. and the nominal pulp retention time is in excess of 16 hours. After leaching, the pregnant solution is separated from the solids in an eight-thickener CCD washing circuit. The underflow from each of these 60-foot-diameter thickeners is controlled by a nuclear density gauge which is coupled with a variable-speed centrifugal pump.

Ion Exchange and Uranium Product Precipitation

The uranium and vanadium in the pregnant liquors are separated by an ion-exchange operation. An anionic exchange resin is used in a standard-column ion-exchange circuit.

The liquors from the leach circuit are stored in large wooden tanks where the final pH adjustment is made, and any pentavalent vanadium


CCD WASHING CIRCUIT
H_2SO_4+Steam

ions in solution are reduced to the quadrivalent state with sulfur dioxide. The quadrivalent vanadium will not load on the anionic resins used in the columns.

A five-column system is used at the Uravan plant. The uranium which is loaded on to the resin as an uranyl sulfate complex is eluted with an acidified brine solution. This pregnant brine solution is precipitated with ammonia, and the yellow-cake product is then filtered in plate and frame presses and dried in a multiple-hearth dryer.

The vanadium ions pass on through the ion-exchange column and are recovered in the subsequent vanadium processing circuits.

Vanadium Recovery

The vanadium is recovered from the ion-exchange uranium-barren liquor by oxidizing the vanadium to the pentavalent state with sodium chlorate and then precipitating the vanadium as a "ferric vanadate." The ferric vanadate forms when the pH is raised with an alkaline reagent and the solution is heated. The ferric vanadate, probably a mixture of at least several pentavalent vanadium compounds, is then filtered, mixed with soda ash, and roasted in a multiple-hearth furnace. The calcine is quenched into an alkaline circuit where the vanadium goes into solution. The impurities, such as iron, remain in the residue. The soluble values are washed from this residue in a thickener circuit. The ferric vanadate also can be treated in an alternate alkaline-leach circuit.

Vanadium Precipitation

The clarified liquor from the roasting or alkaline leach circuits is routed to the vanadium precipitation circuits. This vanadium can be precipitated as a sodium hexavanadate (red cake) by the standard technique of adding sulfuric acid and heating to about 80° to 85°C. Enough acid is added to reach the isoelectric point which is in the range of 2.5 to 2.8 pH. The small floes which form agglomerate into small spheroidal particles which filter readily. Nutsche filters are used to separate the red-cake solids from the mother liquor, and the cake is also washed in these filter-bottom tanks.

This red cake is purified by redissolving it and reprecipitating a second vanadium product. This material is again collected and washed on the Nutsche filters and then dried and fused in a multiple-hearth furnace. The molten product is flaked on a chilled casting wheel and packaged in steel drums for shipment.

The second-stage precipitation removes most of the alkali present in the initial red cake, and the final fused product is a low-alkali material of approximately 98 percent V>0.>

PROCESS DESCRIPTION AND FLOWSHEET

(Sept. 8, 1961)

Rifle Mill

Operator:	Union Carbide Nuclear Company
Location:	Rifle, Colorado
Rated Plant Capacity:	1000 tpd (for Rifle Complex)
Products:	Fused Vanadium Oxide (plus 98 percent V2OrJ Ammonium Metavanadate (AMV) Uranium Yellow-Cake Product
Process:	Extraction: Salt Roast and Acid Leach Uranium-Vanadium Separation: DEHPA Solvent Extraction J'anadium Recovery: 1. Red-cake precipitation on water-leach liquors. 2. DEHPA solvent extraction on acid-leach liquors. 3. Purification of red-cake products by AMV crystallization process. 4. AMV calcination and fusion.

The Rifle Mill is part of what has been designated the "Rifle Co plex" operation, a complex of metallurgical operations initially consisting of upgrading plants at Slick Rock, Colorado, and Green River, Utah, and the finishing plant at Rifle, Colorado. The Green River upgrader suspended operations early in 1960. The physical-chemical upgrading plant at Slick Rock processes ores tributary to the plant, and operates with approximately a 4 to 1 ratio of concentration. The concentrates are shipped to Rifle by special hopper-bottom trucks. The Rifle plant is a combined salt-roast acid-leach operation. The concentrates and "high" vanadium ores are salt roasted; the "low" vanadium ores are processed for uranium recovery in the "Direct-Acid-Leach" circuit.

The calcines from salt-roast operation are water leached to recover the vanadium that has been converted to sodium vanadate by the salt-roast reaction. The washed tailings from the water-leach section are acid leached to extract the uranium and the nonwater soluble vanadium. The residues from the Direct-Acid-Leach circuit and the acid-leach operation on the salt-roast calcine are washed in an eight-stage thickener circuit.

The uranium-vanadium separation is made on the acid-leach liquors in a solvent-extraction circuit which uses di-2-ethylhexyl phosphoric (DEHPA) acid as the extraction reagent. Vanadium is subsequently-recovered from the uranium-barren raffinate in a second solvent-extraction section. The same reagent (DEHPA) is used in both solvent-extraction sections, and the selectivity is based on pH control and reagent concentration. The uranium-pregnant sodium-carbonate liquors from the stripping units of the uranium-extraction section are precipitated with caustic. The yellow-cake product is dried in a multiple-hearth dryer and packaged for shipment to the Atomic Energy Commission. A sulfuric acid solution is used to strip the loaded solvent in the vanadium solvent extraction circuit. The vanadium is recovered from this relatively high-grade vanadium-bearing liquor either by a red-cake precipitation procedure or by a routing of the liquor back into the salt-roast circuit. A sodium hexavanadate red cake is precipitated from the water-leach liquors which are produced in the salt-roast circuit. The red cake is redissolved in an ammoniacal solution, and a "crude" ammonium metavanadate (AMV) is crystallized from these liquors. The AMV is then calcined and fused to form a plus-98-percent-V2Or, vanadium product.

The 1000-ton-per-day rated capacity of the Rifle complex is based on the total raw-ore feed to both the Rifle and Slick Rock plants. The distribution of the over-all feed rate between the two plants is quite flexible, but normally about 50 to 60 percent of the total tonnage is fed to the Slick Rock upgrader.

A schematic flowsheet of the Rifle operation is shown in Figure 16.

Sampling, Receiving, Crushing, and Grinding

Both run-of-mine ore and Slick Rock concentrates are received at the Rifle plant. The primary crushing and sampling plant for run-of-mine ore is essentially the same as the installation at Uravan. The primary crusher reduces the ore to a minus-2-inch size, and a three-stage bucket sampler with intermediate crushing stages is used to cut the sample. The tertiary sample fraction is passed through a rolls crusher, and the final sample is cut with a Vezin splitter.

The minus-2-inch product from the primary jaw crusher is stored in a surge bin and then fed to an Aerofall grinding mill. The product from this autogenous dry-grinding unit is a nominal minus-14-mesh material. The Aerofall mill is fitted with a direct gas-fired heater; thus simultaneous drying and grinding are possible. High-vanadium and low-vanadium ores campaigned separately through the mill are stored in individual bins.

The Slick Rock concentrates are delivered to the Rifle plant in specially designed hopper-bottom tractor-trailer units. The trucks discharge into a screw-feeder-bucket elevator system which carries the concentrates to the storage bins. Because the concentrates tend to bridge in the bins a modified two-level table feeder is used to provide a controlled feed rate from the bins.

Salt Roasting

The salt-roasting operation is carried out in a rotary kiln on a pelletized feed. The roast calcine is quenched and ground to at least minus-

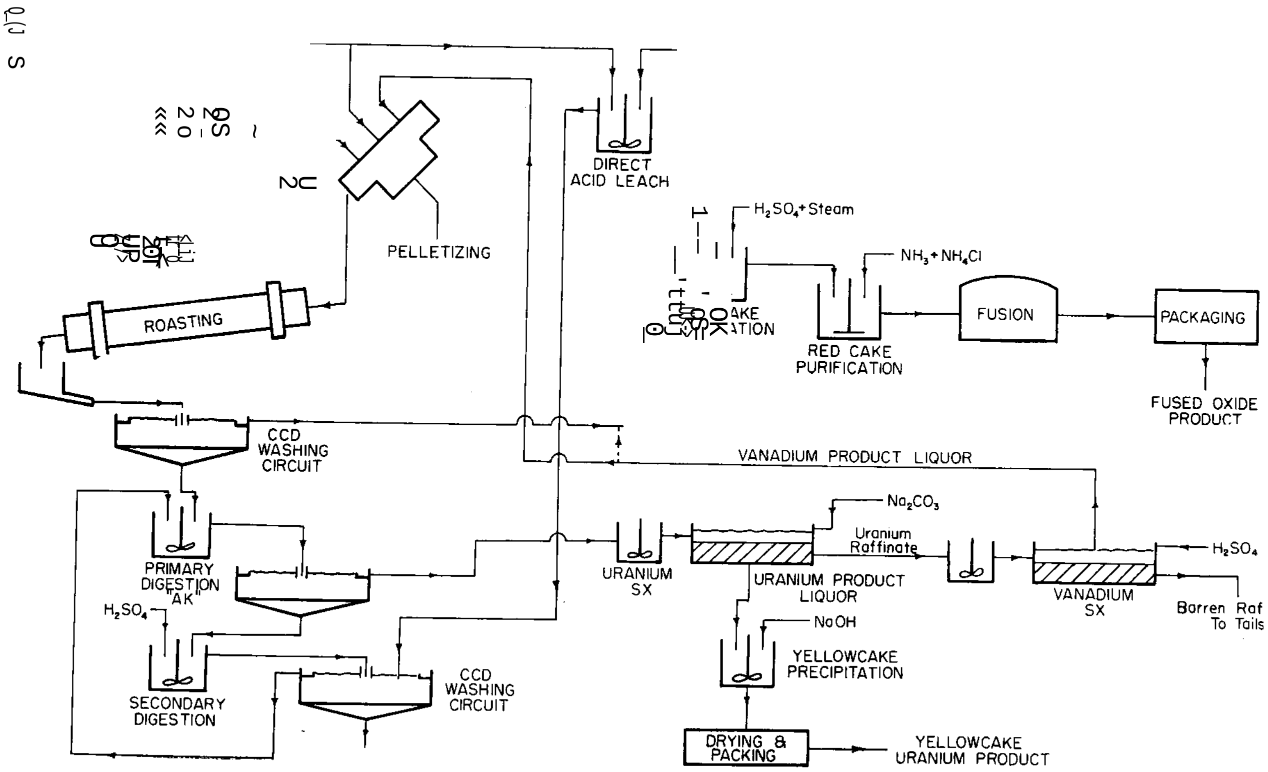


Figure 16. Process Flowsheet, Rifle Mill.
Union Carbide Nuclear Co. (Sept. 8, 1961).

14 mesh. The ground calcines are leached and washed in a combination thickener-filter circuit.

Because the uniformity of the feed rate to the kiln is an important operating variable, the feed rates of the various feed streams are carefully controlled. Salt, concentrates, and minus- 14-mesh ore are fed to a pelletizing unit to agglomerate the mixture and to provide a kiln feed with minimized dusting characteristics. Either water or a stream of the pregnant strip liquor from the vanadium-solvent-extraction circuit is used as the agglomeration liquid. A saucer-type pelletizer is used.

The feed rate to the kiln is dependent upon the type of material being fed to the kiln. The retention time in the kiln varies from about 4 hours to 6 hours, and the maximum bed temperature is near the classical 820° to 850 C range for vanadium-salt-roast operations. The off gases from the kiln pass through a dry dust collecting unit, and then the residual dust and hydrochloric acid generated by the salt-roast reaction are removed by a venturi-type wet scrubber. The dilute acid is clarified in a thickener and used in the Direct-Acid-Leaching circuit.

The pelletized calcines which discharge from the kiln are quenched into a water circuit and ground in a semi-open circuit-classifier ball-mill combination. The rapid leaching reaction obviates the need of leaching tanks. The leached calcines are washed in a circuit consisting of two thickeners and a stage of vacuum drum filters.

The vanadium-pregnant water-leach liquor which contains about 15 grams of Vo05 per liter is pumped to storage tanks near the vanadium-precipitation section.

Acid Leaching Circuits

The Rifle plant has two leaching circuits. One circuit, the Direct Acid Leach, treats the uranium ores which contain relatively low concentrations of vanadium. The second circuit, a two-stage leaching operation, handles the water-leached roast calcine and also provides part of the neutralization required to obtain the optimum acidity for the subsequent solvent-extraction separation of uranium.

Ores passing through the direct-acid-leach circuit are leached for at least 10 to 12 hours. The pulps in this circuit may be heated by steam sparging. As mentioned previously, the HC1 recovered in the kiln scrubbers is used in the Direct-Acid-Leach circuit.

As is shown in the flowsheet, the washed water-leached calcines are contacted in the primary digestion stage with the strong acid solutions from the Direct Acid Leach and the Secondary Digestion. The purpose of this leach contact is to partly neutralize the acidity of the leach liquors and to produce a liquor with a pH of about 1.0. This acidity is near the optimum for the subsequent solvent-extraction operation. At the Rifle plant this primary digestion is known as the "acid kill" (AK) step. A liquor-solids separation on the pulp from the A. K. contact is made in a thickener and the overflow is pumped to storage tanks near the solvent-extraction section.

The pulps from the Direct-Acid-Leach circuit and the calcine-acid leach circuit combine, and the solids are washed in an eight-unit thickener circuit. Nuclear density gauges which control variable-speed centrifugal pumps are used to control the thickener underflows.

Uranium Solvent Extraction

The separation of the uranium and vanadium in the acid-leach liquors is made with a solvent-extraction operation. A 0.1 molar solution of di-2-ethylhexyl phosphoric acid (DEHPA) in kerosene is the recirculating liquid ion-exchange reagent used. A sodium carbonate solution is used to strip the uranium from the loaded solvent.

Before the actual extraction operation, the final acidity adjustment is made to approximately 1.0 pH, and the oxidation-reduction potential is adjusted with powdered iron to assure that all of the iron is in the ferrous-ion state. Ferric ion will load on the solvent and reduce extraction efficiency and tend to contaminate the final uranium product.

The pregnant uranium-bearing solvent is stripped with a sodium carbonate solution, and after clarification a yellow cake is precipitated by the addition of caustic. The precipitate is filtered, washed, dried, and packed in barrels for shipment to the Atomic Energy Commission.

Vanadium Solvent Extraction

The raffinate or uranium-barren liquor from the uranium solvent extraction section is processed through a second solvent-extraction operation to recover the vanadium in this acid solution. The same DEHPA reagent is used for this recovery, but the reagent concentration is approximately 0.4 molar. Also, the pH of the acid liquor is adjusted to near 2.0 to increase the extraction coefficient of this solvent for vanadium.

The vanadium is stripped from the pregnant solvent with a 12- to 15-percent sulfuric acid solution. This vanadium-product liquor can either be oxidized and processed into a red cake or recirculated to the pelletizing operation on the salt-roast kiln feed. The salt-roast operation converts the vanadium to a water-soluble form, and the vanadium is recovered into the water-leach liquors.

The acid-stripping operation does not completely remove iron and other contaminants from the solvent, and part of the solvent is passed through a clean-up or regeneration stage where the contaminants are removed. If not removed, the contaminants soon build up in the recirculating solvent and vanadium extraction drops off rapidly.

Vanadium Precipitation

The final vanadium products are produced by a combination of red-cake precipitation and ammonium metavanadate crystallization techniques.

The water-leach liquors from the salt-roasting operation are heated and acidified to precipitate a standard sodium hexavanadate red cake, which is filtered and washed on filter-bottom tanks.

As mentioned previously, a red cake can also be made from the acidic strip solutions produced in the vanadium solvent-extraction circuit. Because the vanadium in these liquors is in the quadrivalent state, the vanadium must be oxidized to the pentavalent state before a red cake can be precipitated. This oxidation can be accomplished by adding sodium chlorate and heating the liquor to approximately 50 °C. The oxidized liquors are neutralized to 2.0- to 2.5-pH range with soda ash and heated. The red cake is filtered and washed on the Nutsche filters.

After the filtration and washing are completed, the red cake is redissolved in an ammoniacal solution and the residual solids are separated from the liquor by decantation and filtration. The "crude" ammonium metavanadate is crystallized from these polished liquors by adding ammonium chloride and cooling the solutions. The crystalline AMV is filtered on vacuum pan filters and subsequently calcined and fused in a multiple-hearth furnace. The fused vanadium pentoxide is flaked on a chilled casting wheel and packaged in steel drums for shipment.

A high-purity ammonium metavanadate is also produced at the Rifle Plant. This material can be formed either by special selection and handling of the liquors from the red-cake dissolution or by retreatment of the "crude" AMV. The high-purity AMV is air dried and packaged in fiberboard drums.

PROCESS DESCRIPTION AND FLOWSHEET

(Aug. 11, 1961)

Durango Mill

Operator:	Vanadium Corporation of America
Location:	Durango, Colorado
Rated Plant Capacity:	500 tons per day
Products:	Fused Vanadium Oxide (90 percent V205 approximately) Dried Red Cake Uranium Oxide
Process:	Extraction: Salt Roast-Carbonate Leach-Acid Leach Uranium-Vanadium Leach Separation: Synthetic-carnotite precipitation plus a soda-ash fusion of the synthetic carnotite. Vanadium Recovery: 1. Red-cake precipitation 2. Drying or fusion of the red cake

The Durango Mill (initially converted from a lead-zinc smelter operation to vanadium production in 1941) uses the salt-roast soda-ash-leach process. Uranium-vanadium ores and concentrates are mixed with salt and roasted. The calcines are quenched into a sodium carbonate liquor. The uranium and part of the vanadium are recovered as a synthetic-carnotite yellow cake. This precipitate forms when the alkalinity of the oxidized liquor is reduced with sulfuric acid and the solution is heated. The uranium-vanadium separation on this yellow-cake product is made by fusing the material with a soda ash-sawdust mixture and water leaching the resulting melt after it is cooled. The vanadium is taken into solution, and the uranium remains as a water-insoluble oxide compound, UnOs-

The vanadium-bearing liquors are processed using standard red cake precipitation procedures. The red cake is either fused or dried before marketing.

A schematic process flowsheet of the Durango operation is shown in Figure 17. (See fold-out sheet.)

Crushing, Sampling and Grinding

Ore and concentrate from the upgrader at Monument Valley, Arizona, are processed at the Durango Plant. The upgrader is operated by the Vanadium Corporation of America.

Ores received at the Durango Mill are put through the primary crusher and then sampled according to A.E.C. contract requirements. Ores containing more than about 5 percent moisture are dried before the subsequent dry-grinding operation. The crushed ore is ground to a nominal 14-mesh grind in dry-rod mill circuits.

The dried concentrate from the upgrader is trucked to the Durango plant and is stored in either stockpiles or bins.

Salt Roasting — Carbonate Leach

The Durango mill has six multiple-hearth roasters. Ore and concentrates are roasted separately. The salt addition to the ore is equivalent to about 5 percent of the ore weight; approximately a 14-percent salt addition is made to concentrates. The top bed temperature in the roasters is about 840°C.

The off-gases from the roasters which contain both entrained dust and HCl are passed through a wet scrubber. The scrubbing liquor is recirculated through the scrubber to build up acid concentration. A solids-liquid separation is made within the scrubber system, and the clarified liquor is pumped to the acid-leaching circuit. The solids slurry effluent from the scrubbing unit is neutralized with soda ash, and the solids are recirculated to the roasting operation. The liquor which is filtered from the neutralized slurry is pumped to the carbonate-leaching circuit.

The salt-roasted ore calcines are quenched into an alkaline leach liquor held at about a pH of 11 by the addition of soda ash. The quench slurry is pumped to percolation leach tanks where the solids are leached and washed before being pumped to the carbonate tails ponds.

The salt-roasted concentrate calcines are also quenched into an alkaline-leach liquor. After partial dewatering the concentrate calcines are washed on a series of three drum filters. The discharge from the third filtration-washing stage is pumped to the tailings ponds.

Uranium and vanadium are taken into solution during the carbonate leaching of the calcines. The uranium-vanadium-product liquors from both the percolation and filtration washing circuits are routed to the synthetic carnotite precipitation section.

Uranium-Vanadium Separation and Uranium Recovery

The uranium-vanadium separation used at the Durango mill is based on a combination of precipitation, fusion, and leaching techniques.

The uranium is precipitated from the carbonate-leach liquors as a synthetic carnotite "yellow cake." This yellowr cake, a sodium uranyl vanadate, forms when the pH of the hot carbonate liquors is adjusted to about an 8 pH with sulfuric acid. The carbonate strip liquors from the solvent-extraction circuit are also processed in this yellow-cake precipitation circuit.

After filtration and washing, the yellow cake is mixed with soda ash, sodium sulfate, sawdust, and fuel oil. This mixture is charged into a small reverberatory furnace and fused. The melt is tapped into cooling pans and subsequently broken into small chunks before being charged to a leaching tank. The vanadium is converted to a water-soluble compound during the fusion, and the uranium forms the equivalent of a U308 oxide. The soluble vanadium is washed from the uranium oxide product by a combination of decantation and filtration steps. The final uranium product which has an analysis of greater than 80 percent U308 is dried and packed for shipment.

Acid Leaching-Solvent Extraction

The tailings from the carbonate leaches on the roaster calcines contain residual uranium and vanadium that are quite readily soluble in dilute acid solutions. The tailings are reclaimed from the carbonate tails ponds and leached with a combination of scrubber acid and H0SO4 in percolation leach tanks.

The pregnant uranium-vanadium-product liquors from the acid leach are oxidized with KMn04 and solvent extracted with a combination organo-phosphate-amine extractant. The uranium and vanadium are coextracted by this reagent combination which contains approximately 2 percent by volume of di-2 ethylhexyl phosphoric acid and 6 percent by volume of trifatty amine. A kerosene carrier or diluent is used.

The uranium and vanadium are co-stripped from the pregnant solvent with a sodium carbonate solution. After clarification the strip liquor is pumped to the synthetic-carnotite precipitation section.

In this plant, solvent extraction is not used as a uranium-vanadium separation technique, but it functions as a method for recovering uranium and vanadium from acidic liquors and concentrating them in a carbonate liquor amenable to the synthetic-carnotite precipitation scheme.

Vanadium Precipitation

The vanadium in the filtrates from the synthetis-carnotite precipitation is recovered as a normal sodium hexavanadate red cake. When the clarified liquors are heated and acidified with sulfuric acid, the granular red-cake precipitate forms. This product is filtered and washed on Nutsche-type filters. An ammonium sulfate solution, used for part of the washing cycle, represses redissolution of the red cake and also can help to reduce the alkali content of the red cake by displacement of the sodium with ammonia ions.

The red cake is either fused in batch melting furnaces or dried without fusion. The fused and flaked oxide contains 88 to 90 percent VoOr,

Other Mills

The vanadium produced at the Shiprock and Edgemont mills is a byproduct of the uranium-extraction operations at these plants. Both mills use acid-leaching circuits. The uranium-vanadium separation is made by solvent extraction at Shiprock and by a combination ion-exchange solvent-extraction method at Edgemont.

Burwell n" has given the following description of these operations:

> "At the Shiprock plant of the Kerr-McGee Uranium Company, the sulfuric acid tail liquors from uranium extraction containing vanadium in the reduced valency (VO4) are loaded on an organic solvent at a pH of 1 to 2. The organic is then stripped with 5 pet sulfuric acid. The strong acid strip liquor is then stripped of its vanadium by heat and oxidation, yielding vanadic acid, HVOd, or acid red cake. As the acid strip liquor contains iron and phosphorus, the recovery of vanadium oxide is carried on at a high acidity which results in the phosphorus and the largest part of the iron remaining in the acid raffinate. This is fed into the uranium leach circuit carrying the unprecipitated VjO-;. A portion of the V>0.-, then recycles through the uranium leach circuit.
>
> A similar circuit is in operation at Edgemont, South Dakota. at the plant of Susquehanna-Western, Inc."

The Minerals Engineering Company operation at Salt Like City. Utah.

is the first commercial installation designed specifically to recover vanadium from the ferrophosphorus slags produced during the manufacture of elemental phosphorus. These slags which are primarily iron-phosphide compounds contain the equivalent of 7 to 10 percent V^O.-,. The slag is ground, mixed with salt, and roasted in a multiple-hearth roaster. The vanadium is taken into solution in a water-leaching circuit and is recovered from the liquor via an amine SX circuit as AMV. This product is subsequently decomposed and fused to form a high-grade oxide product. This new flowsheet uses some of the very latest technology developed in the vanadium-processing industry.

METALLURGICAL PROBLEMS AND RESEARCH REQUIREMENTS OF THE INDUSTRY

It is not uncommon for a Colorado uranium-vanadium mill to receive its ore supply from 25 or more different mining operations. The mineralogical composition of the ores can vary considerably, and these differences are probably the main source of metallurgical or chemical problems in the Colorado mills. Visits at the various milling operations did not disclose any specific metallurgical problem common to all of the plants. Each mill has difficulties which appear to be associated with the flowsheet and ore supply for that particular operation. The metallurgical characteristics of the ore from a single mine can change considerably during the life of the operations. For example some of the highly oxidized carnotite-type ores are considerably easier to salt roast than the more reduced materials produced from the deeper levels of the same mine.

The processing conditions used in the Colorado vanadium operations sometimes are a compromise among conflicting objectives. Laboratory and plant experience have shown that the optimum processing conditions can vary considerably for individual ores. The best roasting temperature and retention time for an oxidized ore may be substantially different than for a less oxidized ore from the same general area. An ore-blending program can help to smooth out operating variations, but this technique does have both cost and metallurgical limitations. The amount of rehandling that is economically possible is of course limited, and the composition of the blend can have positive and negative effects. A blend containing a good roasting ore and another material with only a moderate roasting amenability can at times show a better roast conversion than would be predicted by the weighted average response of the individual components. It is also true, however, that some blends such as those containing organic materials can show a very poor roast amenability even though some of the components are good salt-roast ores.

Much of the technology of vanadium processing has developed as an art. In many ways the empirical approach has been highly developed, but future processing improvements will probably depend upon a better understanding of vanadium chemistry.

Basic Research

There are at least two primary reasons why the chemistry of vanadium is among the least quantified facets of inorganic chemistry:

1. The difficult and complex behavior of vanadium.
2. The relatively small size of the vanadium industry which limits the amount of money available for basic research.

The lack of adequate identification criteria for vanadium compounds and ionic associations in acidic solutions has been a disadvantage to the vanadium industry. For example, the amount of data on the x-ray diffraction properties and infrared adsorption characteristics of vanadium compounds is limited. X-ray diffraction index data and infrared spectra on vanadium compounds could be helpful for future process improvements. Other types of physical and chemical data apparently are also unavailable for many vanadium compounds.

Applied Research

The problems and process-improvement studies of vanadium milling operations are unique to each plant. Thus, industry feels that this type of applied research is an individual requirement and responsibility of each operation.

Some types of applied research such as development of improved analytical procedures and product development studies could be beneficial to the entire industry. The available analytical methods have served the industry well, but as extractions have improved and product grades have increased, the limit of accuracy on the analytical determinations becomes more critical. As in any process industry, fast, accurate, analytical methods that can be used for plant control tests are valuable. Applied research on new uses for vanadium would also be important to the industry because currently 80 to 90 percent of the output is used in the production of steel. A wider range of markets for vanadium would stabilize the present vanadium milling industry and would also be an encouragement for future growth.

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A SELECTED ANNOTATED BIBLIOGRAPHY OF VANADIUM PROCESSING

The references in this bibliography are arranged in reverse chronological order under each of the following classifications or sections:

Section	
1.00	Mineral Dressing
2.00	Roasting Processes
3.00	Acid Leaching
4.00	Acid Pugging and Baking
5.00	Alkaline Leaching
6.00	Ion Exchange
7.00	Solvent Extraction
8.00	Vanadium Precipitation
9.00	General Vanadium Chemistry
10.00	Metal and Alloy Production
11.00	Chemical and Ceramic Uses
12.00	General Information and History

SELECTED ANNOTATED BIBLIOGRAPHY OF VANADIUM PROCESSING

Section 1.00 —Mineral Dressing

1.01 Process for Concentrating Carnotite.
Dunn & Bradley
U. S. Pat. 2,562,024, Feb. 24, 1951
An attrition process is described

1.02 Ore Scrubbing Apparatus
A. J. Weinig
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1.03 Concentration of Vanadium Ores by Attrition Followed by Froth Flotation.
A. J. Weinig
U. S. Pat. 2,464,313, March 15, 1949

1.04 Unusual Metallurgy.
Mining World, vol. 6, no. 9, Sept. 1944, pp. 23-27
The 1944 operations of the gravity concentration, flotation. and chemical processing circuits for vanadium recovery at the Mammoth St. Anthony mill near Tiger. Arizona, are described in considerable detail.

1.05 Dry Concentration of Carnotite Ores.
Rees, Dunn, and Sproul
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Ecjuipment for dry grinding and scrubbing is described.

1.06 Process for Concentrating Oxidized Ores by Means of Froth Flotation.
G. Gutzeit
U. S. Pat. 2,125,631, Aug. 2, 1938

1.07 Concentration Method
R. G. Osborne
U. S. Pat. 2,136,726, Nov. 15, 1938
A dry attrition process is described.

1.08 Recovering Zinc and Vanadium at the Rhodesian Broken Hill Plant.
T. R. Pickard
Eng. & Min. J., vol. 136, no. 10, Oct. 1935, pp. 489-493.
A process flowsheet and description of the gravity concentration and chemical processing of the descloizite and vanadinite minerals of the Broken Hill deposit is presented.

1.09 Vanadium Recovery at Broken Hill.
Eng. & Min. J., vol. 131, no. 6, March 23, 1931, pp. 259.
This article gives a description of Fe-Zn vanadate precipitation process which was in use at Broken Hill during 1931.

1.10 Method of Concentration of Ores.
O. J. Adams
U. S. Pat. 1,070,313, Aug. 12, 1913.
A combination physical-chemical upgrading process is described.

Section 2.00 — Roasting Processes

2.01 A Mechanism Study ol the Formation of Sodium Vanadate Compounds Under the Conditions of the Salt Roast Process.
W. H. Dresner
AIME Preprint 61B48, Feb. 1961

2.02 Calcination of Vanadium Slags in a Fluidized Bed.
Slotvenski and Potapov
Stal., no. 4, 1960, pp. 327-329
From English Abstracts of Selected Articles from the Soviet Bloc and Mainland China Journals, Feb. 1961
A description of laboratory studies of a fluid bed salt roast on a slag containing 9.4 percent V»0.-,.

2.03 Studies on the Extraction of Vanadium Pentoxide from Vanadium Bearing Titaniferous Magnetite Ores of Bihard and Oressa (India).
Roy and Bhatnager
N.M.L. Technical Journal, May 1960, pp. 27-31
A salt-roast-water-leach process is described.

2.04 Process for Extracting Vanadium Values from Ores, Slags, Concentrates and the Like.
Dunn, Mayer, O'Brien
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A roast process using salt plus an active phosphorous compound is described.

2.05 Titaniferous Magnetite Treatment.
T. P. Campbell
U.S. Pat. 2,417,101, Nov. 11, 1957
An alkali roasting process is described.

2.06 Salt Roast, Hot Water Leach, and H^.SOj Precipitation for Recmery of V2Or, (at Otanmaki).
Martti Merenmies
Min. World, vol. 19, no. 4, April 1957, pp. 55
Mr. Merenmies gives a description of the high temperature Na2S04 roast process used to extract vanadium from the magnetite concentrates at Otanmaki, Finland.

2.07 Vanadium Salt Roasting Studies.
Alan Stanley
ACCO-51, 1954

2.08 Tristage Crystallization Process for Utilizing Western Ferrophosphorus.
Banning, Anable, and Rasmussen
J. of Metals, March 1953, p. 425
The article gives a description of the roasting and subsequent separations processes for vanadium recovery from the vanadiferous Western USA phosphate ores.

2.09 Soda Sinter Process lor Treating Low Grade Titaniferous Ores.
MacMillan, Heindl, and Conley
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2.10 Treatment of Titaniferous Magnetite Ores from Iron Mountain, Wyoming.
Bach, Chundgren, and Paterson
U.S.B.M. RI 4902, 1952
An alkaline roast process is described.

2.11 Recovery of Vanadium from Titaniferous Magnetite.
Cole and Breitenstein
J. of Metals, vol. 3, no. 12, Dec. 1951, pp. 1133-1137

This article describes the laboratory and pilot-plant work on the recovery of vanadium from the Tahawas, New York, magnetites.

2.12 Process of Recovering Vanadium from Western Phosphates.
Banning and Rassmussen
U.S.B.M. RI 4822, 1951
The process is a combination of beneficiation, smelting, roasting, and leaching operations. Both phosphorus and vanadium are recovered.

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MacMillan, Dinneu, and Conley
U.S.B.M. RI 4638, 1950
Laboratory tests on sintering with carbon and soda ash to produce metallic iron and soluble titanates are discussed.

2.14 The Recovery of Uranium and Vanadium from Low Uranium Process Precipitates.
G. W. Clevenger
MITG-238, 1950

2:15 Studies of Recovery Process for Western Uranium Bearing Ores.
Part I. A Critical Examination of the Salt-Roast, Acid-Leach Process for Western Uranium Ores.
Saine and Brown
Y-499, 1949

2.16 Treatment of Idaho-Wyoming Vanadiferous Shales.
Ravitz, Nicholson, and Chindgrew
AIME Tech. Publication, No. 2178, June 1947
A salt-roast process on shales containing 1 percent VoOs and 2 or 3 percent Po03 is described.

2.17 Process of Treating Iron Ores Containing Chromium and Related Oxides.
D. Gardner
U.S. Pat. 2,409,428, Oct. 15, 1946
A roasting process using Ca(OH)2 is described.

2.18 Recovery of Vanadium from Vanadium Bearing Materials.
L. G. Jenness
U.S. Pat. 2,270,444, Jan. 20, 1942
A roasting process to increase vanadium extraction during subsequent chlorination or acid leaching is described.

2.19 Recovery of Vanadium from Vanadium Bearing Materials.
L. C. Jenness
U.S. Pat. 2,270,444, Jan. 20, 1942
A process consisting of fusion and roasting followed by leaching or chlorination is described.

2.20 Extraction of Vanadium Values from Vanadium Bearing Materials.
Robertson. Dunn, and Sproul
U.S. Pat. 2.257,978, Oct. 7, 1941
An oxidizing-roast, water-leach, acid-leach process is described.

2.21 Process for Recovering Vanadium and Uranium from Ores.
H. D. Brown
U.S. Pat. 2,217,665, Oct. 15, 1940
A roasting process is described.

2.22 Extracting Values from Complex Ores of Vanadium and Uranium.
H. McCormack
U.S. Pat. 2.176,609, Oct. 17, 1939
An ammonium sulfate roasting process is described.

2.23 Process of Extracting Vanadium from Vanadium Bearing Silicate*.
B. Mayer
U.S. Pat. 2,183,027, Dec. 12, 1939
An oxidizing-roast-acid-leach process for slags is described.

2.24 Treatment of Titanium and Iron Containing Materials.
B. D. Saklatwalla
U.S. Pat. 1,845,342, Feb. 16, 1932
A chlorination process is described.

2.25 Recovery of Vanadium from Ores or Compounds.
B. D. Saklatwalla
U.S. Pat. 1,779.856, Oct. 28, 1930
A chlorination process is described.

2.26 Vanadium in Iron Ores and Its Extraction.
R. VonSeth
Eng. & Min. J., vol. 120, no. 2, July 1925, pp. 51-55
A description of a salt roast process for slags produced when a blast-furnace product is blown in an acid converter.

2.27 Treatment of Vanadium Ores.
M. J. Udy
U.S. Pat. 1.513,200, Oct. 25, 1922
A fusion process using an alkali plus a sulfur-bearing material as reagents is described.

2.28 Method of Treating Complex Carnotite Ores.
Danforth, Samuels, Martersteck
U.S. Pat. 1,126,182, Jan. 26, 1915
A roasting process is described.

2.29 Process of Producing Copper, Lead or Iron Vanadate from Vanadiferous Ores.
W. F. Bleecker
U.S. Pat. 1,015.469, Jan. 23, 1912
A salt-roasting process followed by water leaching and acid leaching is described. The vanadium values are recovered from the water-leach or acid-leach solutions as iron. lead, or copper vanadates.

Section 3.00 — Acid Leaching

3.01 Process Development Studies for Lukachukai Ores.
D. C. McLean
ACCO-64, 1955
A roasting and leaching process for the recovery of uranium and vanadium is described. Ion exchange is used for the uranium-vanadium separation.

3.02 Nonaqueous Extractive Methods for Western Uranium Ores.
Ewing, Pobereskin. Kimball, and Bearse
BMI-271, 1953
Studies on the HCl-methanol leaching process are described.

3.03 Studies of Recovery Processes for Western Uranium Bearing Ores.
Part II — Direct Acid Leaching of Western Uranium Ores
Saine and Brown
Y-499, Oct. 1949

3.04 Process for Removing Lime from Ores.
Hatherell and Garbutt
U.S. Pat. 2,369,345, Feb. 13, 1945
A leach with CaCl2 plus HC1 is discussed.

3.05 Process for the Recovery of Uranium and Vanadium from Carnotite Ores.
H. Fleck.
U.S. Pat.'2,199,696, May 7, 1940
An acid-leaching process is described.

3.06 Method of Treating Vanadium Ores.
G. A. Hatherell
U.S. Pat. 2.197,241, April 16, 1940
An acid-leaching process is described.

3.07 Process of Treating Ores.
J. S. Potter
U.S. Pat. 2,180,692, Nov. 21, 1939
An acid-leaching process is described.

3.08 Process of Working Ores of Vanadium and Uranium.
U.S. Pat. 2,176,610, Oct. 17, 1939
An acid-leaching process is described.

3.09 Notes on Extraction and Recovery of Radium, Vanadium, and Uranium from Carnotite.
H. A. Doermer
U.S.B.M. RI 2873, 1928
A nitric acid-leach procedure is described.

3.10 Process for Extracting Vanadium from Its Ores.
Koenig
U.S. Pat. 986,180, Sept. 21, 1910
An acidic-pressure leach method is described.

Section 4.00 — Acid Pugging and Baking

4.01 The Technique of Acid Pugging and Curing of Ores.
D. C. McClean
TID-5156, 1953

4.02 Process of Obtaining Uranium and Vanadium from Their Ores.
Nye and Demorest
U.S. Pat. 2,173,523, Sept. 19, 1939
An acid-cure process using dilute acids is described.

Section 5.00 — Alkaline Leaching

5.01 Method for Treating Vanadium and Uranium Ores and the Like.
B. Burwell
U.S. Pat. 2,630,369
An alkaline-leach process is described.

5.02 Metallurgical Process.
R. F. Meyer
U.S. Pat. 2,086,570, July 13, 1937
A "caustic cure" process is described.

5.03 Process for the Extraction of Uranium and Vanadium from Certain Ores.
W. F. Bleecker
U.S. Pat. 1,438,357
An alkaline-leach process is described.

5.04 The Extraction of Vanadium from Carnotite and Vanadiferous Sandstone Concentrates.
S. Fischer
Met. & Chem. Eng., vol. 10, Aug. 1912, pp. 469-471
A caustic-cure process is described.

5.05 Process of Treating Ores.
Haynes and Engle
U.S. Pat. 808,839, March 20, 1905
An alkaline-leach process using NaOH to precipitate the uranium and CaO to precipitate the vanadium is described.

Section 6.00 — Ion Exchange

6.01 Anionic Exchange Behavior of the Vanadium (IV) Thiocyanate Complex. Separation of Vanadium from Aluminum.
J. S. African Chem. Inst., vol. 13. 1960, pp. 82-88

6.02 Separation of Uranium and Vanadium with the Aid of Anion Resins.
Morachevsky and Gordeyera
Vestnik Leningrad Univ., no. 10, 1957, pp. 148-151
Translated from Referat Zhur. Met., no. 3. 1958

6.03 Development of an Ion-Exchange Process for the Recovery of Vanadium.
McLean, Hollis, and Eisenhauer
ACCO-63, 1954
A description of an ion-exchange process for vanadium is given. Both column and R.I.P. data are presented.

6.04 Recovery of Vanadium by Ion Exchange.
Abrams and Izzo
ACCO-53, July 1954

6.05 The Electrolytic Recovery of Uranium and Vanadium from Carbonate Leach Liquors.
J. Saunders
RMO-2525, 1953
Methods for obtaining uranium and vanadium from carbonate leach liquors by ion-exchange are described.

6.06 The Exchange of Vanadium (II) and Vanadium (III) Ions in Perchloric and Sulfuric Acid Solutions.
King and Garner
J. Am. Chem. Soc, no. 74, July 1952, pp. 3709-3710

6.07 The Kinetics of the Vanadium (III)—Vanadium (IV) Exchange Reaction in Aqueous Perchloric Acid Solutions.
Furman and Garner
J. Am. Chem. Soc, no. 74, July 1952, pp. 2333-2337

6.08 Uranium Recovery from Miscellaneous Materials.
R. H. Bailes
Dow-40, Dec. 1950
Ion-exchange recovery of uranium and vanadium is described.

Section 7.00 — Solvent Extraction

7.01 Liquid Ion-Exchange-Vanadium.
General Mills Inc.
General Mills Inc. Publication CDS-3-60, 1960
The solvent extraction of vanadium with high molecular weight, water insoluble, quaternary ammonium chloride compounds is described.

7.02 Solvent Extraction of Vanadium (and Uranium) from Acid Liquors with Di-(2-ethylhexyl) Phosphoric Acid.
Crouse et. al.
ORNL-2820, 1959

7.03 Raw Materials Process Testing Progress Report of Pilot Plant Section of Jan. 1955.
ORNL-1970, 1956
Amine SX of vanadium from acidic liquors is described.

7.04 Solvent Extraction of Uranium (and Vanadium) from Acid Liquors with Trialkylphosphene Oxides.
Blake, Brown, and Coleman
ORNL-1964, Aug. 1955

7.05 The Extraction and Recovery of Uranium (and Vanadium) from Acid Liquors with Di-(2-ethylhexyl) Phosphoric Acids.
Blake, Brown, and Coleman
ORNL-1903, May 1955

7.06 The Recovery of Uranium and Vanadium from Carnotite Ores by Solvent Extraction.
R. H. Bailes
Dow-93, 1953
An investigation of the recovery of uranium and vanadium acid slurries with dioctyl phosphoric acid is reported.

Section 8.00 — Vanadium Precipitation

8.01 Research and Development Quarterly Report for July-Sept. 1960.

Eldorado Mining and Refining Ltd.
NP-9396, 1960
An outline is presented of various approaches to the problem of vanadium removal from Beaverlodge solution and precipitate.

8.02 Process for Recovery of Uranium and Vanadium from Carbonate Solutions by Reduction-Precipitation.
Ellis and Lindblom
U.S. Pat. 2,807,518, Sept. 1957
Sodium amalgam is used as the reducing agent.

8.03 Precipitation of Uranium and Vanadium from Carbonate Leach Liquors Using Sodium Amalgam.
Dixon, H. E.
Win-16, Sept. 20, 1955

8.04 The Lead Vanadate Precipitation Method for the Recovery of Vanadium from Carbonate Leach Solutions.
Clifford and Huggins
RMO-2619, June 1955

8.05 Electrolysis of Carbonate Leach Solutions.
Huggins, Carlson, Schwien
RMO-2611, Oct. 1955
A summary of batch studies performed on the electrolytic reduction and precipitation of uranium and vanadium in carbonate solutions is presented.

8.06 Summary and Cost Estimates Using Electrolytic Reduction in Selected Flowsheets.
Huggins and Carlson
RMO-2613, April 1954

8.07 Dow Progress Report—Dec. 1953.
Bailes, R. H.
Dow-109, Dec. 1953
Studies of the recovery of uranium and vanadium from leach solutions of carnotite ores are presented.

8.08 Precipitation of Vanadium from Aqueous Vanadate Solutions bv Reduction with Hydrogen.
O'Brien et al.
Can. Min. & Met. Bull., vol. 46, no. 499, Nov. 1953

8.09 The Electrolytic Recovery of Uranium and Vanadium from Carbonate Leach Liquors by Means of Ion Exchange Membranes.
Saunders, Jean
RMO-2525, 1953

8.10 A Preliminary Economic Analysis of the Sodium Amalgam Process.
McClaine and Mohan
RMO-2609, 1952

8:11 Electrolysis of Carbonate Leach Solutions.
Huggins, J. C.
RMO-2607, July 1952

8.12 The Electrolytic Recovery of Uranium and Vanadium from Carbonate Leach Liquors by Means of Ion Exchange Membranes.
RMO-2519

8.13 Electrolytic Recovery of Uranium and Vanadium from Climax Leach Liquors.
Kirk, Paul F.
RMO-2512, 1952

8.14 Vanadium Recovery from Chromate Liquors.
Perren et al.
I & E Chem., vol. 44, no. 2, Feb. 1952, pp. 401-404.
The process is based on the relative solubilities of lead sulfate. lead chromate, and lead vanadate in an 8.5-pH solution.

8.15 Process of Precipitating Hydrous Vanadium Pentoxide.
Dunn, Wallace, and Mayer
U.S. Pat. 2,551,733, May 8, 1951
A two-step precipitation process for producing high-grade red cake is reported.

8.16 Studies of Recovery Processes for Western Uranium Bearing Ores. Part IX, Precipitation of Yellow Cake and of Low Level Vanadium.
AECD-3223 or Y-663, Nov. 1950

8.17 Studies of Recovery Processes for Western Uranium Bearing Ores. Part III, The Recovery of Uranium and Vanadium from Acid Leach Liquors of Carnotite Ores.
Coleman, C. F.
Y-500, Nov. 1949

8.18 Studies of Recovery Processes for Western Uranium Bearing Ores. Part VI. Precipitation of Vanadium Red Cake.
Seeley and Coleman
Y-503, Oct. 1949

8.19 Precipitation of Red Cake from Low Vanadium Acid Sulfate Leach Liquors.
Hollis and McClean
ACCO-45, 1945
A process is described for precipitating the vanadium as ferric vanadate, followed by caustic leaching of the precipitate and reprecipitation as red-cake.

8.20 Vanadium Recovery from Chromates.
VanWirt and Aylies
U.S. Pat. 2,357,988, 1944
A precipitation procedure is described.

8.21 Beneficiation of Vanadium Compounds.
Frick, F. A.
U.S. Pat. 2,357,466, Sept. 5, 1944
Conversion of sodium hexavanadate to ammonium hexavanadate is described.

8.22 Recovery of Vanadium.
Nelson, J. J.
U.S. Pat. 2,357,488, Sept. 5, 1944
A method of recovering vanadium from phosphovanadic acid solutions is reported.

8.23 Oxidized Fractional Precipitation Process on Unreduced Uravan Acid Leach "A" Liquor.
Norton, L. K.
AECD-3760. May-June 1944

8.24 Process for Separating Vanadium from Titanium.
Jenness and Annis
U.S. Pat. 2.230,538, Feb. 4, 1941
Precipitation of vanadium from liquid $TiCl4$ by means of an organic precipitant is described.

8.25 Recovery of Vanadium.
Freck and Woodman
U.S. Pat. 2,193,092, March 12, 1940
A multistage precipitation process for recouping vanadium from leach liquors containing greater than 5 g/1 of phosphorus is described.

8.26 Method of Treating Vanadium Ores and Solutions.
Carpenter, A. H.
U.S. Pat. 1.531,541, March 31, 1925
A precipitation process is described.

8.27 Process for Separating Vanadium from Uranium.
Bleeker, W. S.
U.S. Pat. 1,050,796
A process for selective electrolytic precipitation ol vanadium in the presence of uranium is reported.

Section 9.00 — General Vanadium Chemistry

9.01 The Relationship Between Oxidation Reduction Potential and \ alence State of Iron, Vanadium and Uranium in Sulfuric Acid Leach Liquors.
Toohey and Kaufman
ACCO-60, July 1954

9.02 Chemistry of Vanadium.
Frank, Andrew J.
ACCO-49
A summary of the non-AEC literature on vanadium through 1952 is presented. A bibliography of 93 references is included.

9.03 Preparation of Vanadium Monoxide.
Frandsen, M.
J. Am. Chem. Soc, no. 74, Oct. 20, 1952, pp. 5046

9.04 A Contribution to the Study of Ions of Quadri and Pentavalent Vanadium.
Ducret, L. P.
Ann. Chim. (French), vol. 12, no. 6, Sept.-Oct. 1951, pp. 705-773

9.05 The Technical Chemistry of Vanadium.
Saklatwalla, B. D.
J. of Ind. & Eng. Chem., vol. 14, no. 10, Oct. 1922, pp. 968

9.06 Notes on the Chemistry and Metallurgy of Vanadium.
Bleecker, W. F.
Met. & Chem. Eng., Part I, Dec. 1910, pp. 666-671
Part II, April 1911, pp. 209-213
Part III, Oct. 1911, pp. 499-505

A wide variety of observations on the chemistry of vanadium are presented in Part I. Part II discusses the analytical chemistry of vanadium, and Part III presents data on the metallurgy of vanadium ores.

Section 10.00 — Metal and Alloy Production

(Most of the references in this section were compiled by Sidney J. Bragg, Librarian, Vanadium Corporation of America Research Center, Cambridge, Ohio.)

10.01 Metallothermic Reduction of Vanadium Chlorides.
Block, Brown, and Ferrante
U.S.B.M. RI 5722, 1961

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Merrill, T. W
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Union Carbide Metals Review, Spring, 1959

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J. of Metals, Sept. 1958, pp. 618-21

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Sprankle, A. F.
Metal Bulletin, Nov. 1958, pp. 103-5

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Argonne National Laboratory, 1957, Report ANL-5661

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Deadmore, D. L, et al.
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U.S. Atomic Energy Commission, Sept. 1956

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Armour Research Foundation, WADC Technical Report 52-14.5. Part 3, Jan. 1955

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WADC Technical Report 52-145, Part 4, Project No. B605. Au°. 1955

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Acta Chimica Scandanavia, vol. 8, 1954, p. 624

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Am. Soc. for Metals, vol. 46, 1954, 1136

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Bechtold, J. H.
Am. Soc. for Metals, vol. 46, 1954, p. 397

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Cottrell, C. L. M. et al.
British Welding Journal, Feb. 1954, pp. 82-85

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Steel, 1954, pp. 128-130

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U.S. Atomic Energy Commission, July 1954

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Trans. A.S.M., vol. 46, 1954, p. 1136

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WADC Technical Report 52-145, Part 2, Nov. 1954

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Rostoker, W. et al.
WADC Technical Report 54-312, July 1954

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Vanadium Corporation of America
Reprinted, 1954

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Long, J. R.
Iowa State College, Journal of Science, vol. 27, 1953, p. 213

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Armour Research Foundation, W.A.D.C. Tech. Report No. 52-145 Part I, July 1952

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Montash Chem (German), no. 84, Dec. 1953, pp. 1119-1126

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Am. Soc. for Metals, vol. 43, 1951, p. 935

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ISC-244, Aug. 1951

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Metal Progress, vol. 58, 1950, pp. 315-21

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J. Electrochemical Society, vol. 97, 1950, p. 311

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Westinghouse Engr., no. 10, 175, July 1950

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Richert, Esther, et al.
Office of Technical Services, PB 147 562, Nov. 1960

10.75 Vanadium in Steelmaking, Present and Future.
Johnson, H. E.
Battelle Memorial Institute Report BMI-JDS-136, Aug. 1948

10.76 Recovery of Vanadium and Other Alloys in the Acid Electric Furnace.
Wyman, C.
Elec. Furnace Steel Proceedings, A.I.M.E., 1947

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Dawe, C. N.
Machine Design, Oct. 1941

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Metallwirtschaft, vol. 22, 1934, p. 4054

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J.A.C.S., vol. 52, 1930, p. 2638

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Alexander, Jerome
J. Soc. Chem. Ind., vol. 48, Sept. 1929, pp. 1-13

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Section 11.00 — Chemical and Ceramic Uses

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Vancorum Review, vol. XV, no. 1, 1960, pp. 9-13

11.02 Bibliography of Vanadium Catalysts.
Cosman, C S.
Vanadium Corp. of America Publication, 1960
A bibliography of approximately 300 references, compiled from the chemical abstracts from 1940 through 1954.

11.03 Semiconducting Properties of Some Vanadium Glasses.
Baynton, Rawson, and Stanworish
J. of Electrochemical Society, vol. 104, no. 4, April 1957

11.04 Vanadium and Vanadium Compounds.
Vancorum Review, Spring-Summer 1955

11.05 Vanadium and Some of Its Industrial Applications.
J. Alexander
J. of Soc. of Chem. Ind., Sept. 6 and 13, 1929
Vol. XLVIII, nos. 36 and 37, pp. 871-878 and 895-901

A. Color stabilization for conventional glazes.

11.06 Occurrences of vanadium in clays.
Hammer, A. J.
Ceramic Age, April to Nov. 1955
Vanadium replacement of aluminum in clay-mineral structures is discussed. A comprehensive continued series.

11.07 Method of Providing a Ceramic Base with a Coating of Blue Titania and Article Produced thereby.
Clark, Colin H. W.
U. S. 2,715,593. August 16, 1955
Addition of vanadium oxides is mentioned among others.

11.08 Studies on Vanadium Oxides: I Phase Analysis.
Anderson, George
Acta Chem. Scand., 1954, vol. 8, no. 9, pp. 1594-1606
The book contains 17 references in English.

11.09 X-Ray Studies on Vanadium and Chromium Oxides with Low Oxygen Content.
Schonberg, Nils
Acta Chem. Scand., 1954, vol. 8, no. 2, pp. 221-25
The book contains 12 references in English.

11.10 Crystallization of Quartz Glass.
Katnarskii. I. S. and Degtyareva, E. V.
Doldady Arad Nauk SSSR, 1953, vol. 91, no. 2, pp. 356-58
Studies were made under influence of cations of many compounds including vanadium and anions including VO:...

11.11 Coloration of Glass by Radiation.
Kuan-Han Sun and Kreidl, Norbert J.
Glass Ind.. 1952. vol. 33, no. 10, pp. 511-14, 546
Thermolumincscense is a much more sensitive process than coloration. Photosensitization involves reduction to the elemental state. The behaviors of Mn, Fe, V, Ce. and Ag are cited as samples.

11.12 Oil-Firing from the Viewpoint of the Glass Manufacturer.
Kruszewski, S. and Seddon, E.
J. Soc. Glass Tech., 1951, vol. 35, no. 164, pp. 158-76T
The presence of sulfur or vanadium in the oil causes some coloration of the glass being melted.

11.13 Coating for Artistic Crystallized Stoneware.
Bartoli, Domenico
Ind. Ceram. e Silicati, 1951, vol. 6, no. 5, pp. 25-28
The oxides determining the quality of the surface are mainly ZnO and Ti02, but the anhydrides of W, Mo, V, and U also are good crystallizers.

11.14 Coloured Glasses.
Weyl, W. A.
Soc. of Glass Tech., 1951
This book includes material published to the middle of 1949.

11.15 High-Fire Underglaze Colors: I General Consideration on High-Fire Yellow Colors.
Kanekoto, Fujii and Kinya, Sond.
Bull. Govt. Research Inst. Ceramics (Kyoto). 1950. vol. 4. no. 1. pp. 3-7
Past studies on high-fire underglaze colors are reviewed, and possibilities of making new yellow colors containing V20.-,. V03 among others are discussed. Twenty-four references are cited.

11.16 Physical Properties of Glass.
Stanworth, J. E.
Oxford University Press, London E. C. 4, 1950, 219 pp.. 107 figures.
Part I deafs mainly with the structure of glasses as derived from x-ray diffraction work and the investigation of density. color, fluorescence, and refractivity.

11.17 Mechanism of Coloration of Glass by Tetravalent and Pentavalent Vanadium.
Raisaku, Kiydura; Shoichiro, Kawakubo; Yoshitake, Ito
J. Japan Ceram. Assoc, vol. 57, 1949, pp. 29-30
Ammonium metavanadate 5 percent added to glass K.,0 : CaO • 6Si02. The V4V(V4t + V5+) ratio was estimated by chemical analysis. Visual color was yellowish green and orange yellow.

11.18 Rare-Earth Glasses; I Absorbing Glasses.
Foex. M.
Verres et refractaires, Aug. 1947, pp. 3-18.

Interesting color combinations are obtained with vanadium, tungsten, cobalt, and selenium.

11.19 Oxidation and Reduction of Glasses by Means of Electrolysis.
Rindone, G. E., et al.
State College, Pennsylvania, Glass Science Inc.
J. Am. Ceram. Soc, vol. 30, 1947, pp. 314-19

11.20 Effect of Coloring Oxide Additions on the Spectral Transmission of a Soda-Lime-Silica Glass.
Bachman, George S.
Glass Ind., vol. 28, no. 12, 1947, pp. 630-34, 652.

The effects on ultra violet, visible and infra red transmissions of the addition of coloring oxides to a base glass similar to most commercial glasses were investigated. The coloring oxides of vanadium among others were added in three different proportions. Vanadium was second best as absorber of ultraviolet.

11.21 Colored Glasses; the Colours Produced by Vanadium.
Weyl, W. A.
J. Soc. Glass Tech., vol. 28, 1944, pp. 185-9

Vanadium resembles chromium in its oxidation-reduction characteristics, its tendency to form anions and cations, and the shape of its absorption spectrum. Vanadium glasses can be colorless, yellow to brown, green, or sometimes gray. In extremely basic glasses melted under oxidizing conditions, a colorless glass is obtained absorbing in the ultraviolet. Acid glasses give rise to yellowish-browns indicating polyvanadate formation. Normal green glasses of vanadium coloring are due to vanadic ions. With sulfur as a reducing agent pure blue glasses are obtained with vanadium in the tetravalent state.

11.22 Optical Glass History.
Wheat, W. N.
Optician, vol. 107, no. 277, p. 203-204, 1944, Cer. Abs., vol. 23, no. 166

W. calls attention to the little-recognized work on optical glasses by W. Vernon Harcourt from 1834 to 1860, described in British Assn. Reports for 1871 by Stokes. In addition to the usual glassmaking oxides of the time, Harcourt employed the oxides of lithium, barium, strontium, beryllium, magnesium, aluminum, zinc, cadmium, tin, lead, thallium, bismuth, antimony, vanadium, etc., in combination with phosphates, borates, fluorides, tungstates, molybdates, and titanates. Abbe and Schott knew of this work, and Schott's new glasses owed much to the inspiration of Harcourt's pioneer work.

11.23 Data on Chemicals for Ceramic Use.
Anon
National Research Council Bulletin No. 107, June 1943

Seventeen V salts and the metal are listed as colorants for ceramic materials. The color obtained with each one is given.

11.24 The Effect of Small Amounts of Certain Colouring Oxides on the Colour of a Soda-Lime-Silica Glass.

Preston, Eric

J. Soc. Glass Tech., vol. 25, pp. 5-20, 1941

Vanadium is one-fiftieth as effective as Cr; heating removed tint.

11.25 Glasses colored with Neodymium Oxide and Vanadium Oxide.

Ctyroky, V.

Glastech. Ber., vol. 18, pp. 1-7, 1940. C. A. 34, 3455, 1940

The base glass had the following compn.: 67.0-69.5 percent Si02. 11.6-12.4 percent CaO, 11.6-12.4 percent K20 and 4.0-4.3 percent Na20. The Nd203 and V>05, resp. were added as follows to make the series of glasses studied: 6 percent + 0.01 percent; 5 percent + 0.2 percent; 4 percent + 0.4 percent; 3 percent + 0.6 percent; 2 percent + 0.8 percent; 1 percent + 1 percent; 0.0 percent + 1.2 percent. Polished samples 5 x 10 x 20 mm. were studied photometrically over the range 4000-7000A. By using the av. spectral sensitivity of the eye according to Gibson, Tyndall and McNicholas (C. A. 15, 2968). the transmission coeffs, were recalculated to give values representing the effect on the eye for transmitted sunlight and light from a tungsten lamp. These data are plotted against wave length for both sunlight and the elec lamp.

11.26 Reaction Between Metals and Molten Glass.

Badger, A. E. and Bard, B.

J. Am. Ceram. Soc, vol. 23, pp. 326-8, 1940. C. A. 35, 287, 1941

A series of melts of Na20-Ca0-Si02 glass cullet in contact with various chem elements was made. The heat treatment was for 2 hr at about 1250°. A atm. of H was used to prevent oxidation. Various colors were produced by Cu, Ag, Au, Se, C, and S and Zr. Black fog resulted from melts contg. Ba, Cr or V; gray or black fogs with reddish zones, from melts contg. Mg. Ca, Ti, Mn, Si or Al. A faint blue with large reddish zones was produced by Co. Only slight attack was shown by Fe, Ni, Zn, Cd, Bi, Sn, Pb, Mo and W.

11.27 Effect of Composition and Other Factors on the Specific Refraction and Dispersion of Glasses.

Young, John C. and Finn, Alfred N.

J. of Research of the Na, Bur. St., vol. 25, pp. 759-782, 1940

Vo03 is included in Table 2 — Specific Refraction Factors of Some Oxides as Occurring in Glasses and Crystals. The relation to dispersion to specific refraction and to composition is developed.

11.28 Light-Sensitive Glass and Its Application for Ultraviolet Measurements.

Upton, Lee O.

Glass Ind., vol. 21, pp. 109-12, 1940. C. A. 34, 4242, 1940

Ce-V glasses are well suited to the measurement of ultraviolet light over protracted periods, especially in the wave length range of 3000-3800A. Phosphoric acid and boric acid have a preventive effect on the photo-chem. reaction between CeO, and V205 whereas soda-lime glasses provide a satisfactory base glass for this reaction.

11.29 Vanadium as a Glass Colorant.

Weyl, W. A. and Pincus, A. G. and Badger, A. E.

J. Am. Ceram. Soc, vol. 22, 374-7, 1939

Vanadium, as a glass colorant, acts much like Cr. Ordinarily it leads to green tints which are due to the superposition of the green of trivalent V and the yellow of pentavalent V. Large excess of alkali leads to the formation of colorless vanadates. Under special conditions, solarization may be used to develop the lavendar color of bivalent vanadium. The effect of melting conditions and changes in the base glass composition on the colors is discussed.

11.30 Less Familiar Elements in Ceramic Pigments.

Harbert, C. J.

Ind. Eng. Chem., vol. 50, pp. 770-772, 1938

V salts, especially the metavanadates, are said to be gaining ground as coloring agents in ceramic wares. A V-Sn oxide produces a very stable yellow which is used as a glaze, underglaze, overglaze, or body stain.

11.31 Vanadium in Glass.

Houseman, Charles W.

Vanadium Corp. of America, R. & D. Report, Project P-35, Report No. 1, March 27, 1936

11.32 The Physical Properties of Glasses in Relation to Their Composition. The Transparency of Glass in the Ultraviolet, Visible and Infra-Red Range.

Anon

Vancoram Review, vol. 2, pp. 11-12, 1931

Absorption of ultraviolet glass with V. Ce, Ti, Pb. or Sb in decreasing order of activity are discussed.

11.33 Vanadium in Shatter-Proof Glass.

Anon

Scientific American, vol. 144, 1931, p. 337

11.34 Title Unknown.

Frtiz-Schmidt, M.; Gehlhoff, G. R.; Thomas, N.

Z. Tech. Physik, vol. 11, 1930, pp. 289-326

Included are studies of spectrae absorption of vanadium glasses. (See J. Soc. Glass Tech., vol. 28, no. 128, 1944. p. 188).

11.35 Colored Heat-Resisting Glass.

Taylor, W. C.

U. S. 1,754,182 (April 8, 1930). Vancoram Review, vol. 1. no. 4, 141, July 1930

The patent claims the production of a heat-resisting green glass which shows high transmission of green light and generally good absorption of other parts of the spectrum having a coefficient of linear expansion of less than .0000048, containing lithia, potash, and boric oxide, the ratio of boric oxide to total alkali being less than two to one.

A satisfactory green is produced by the addition of 1.4 percent cupric oxide and .012 percent cobalt oxide to the base glass given above. Chromium or vanadium may be substituted in part for the cupric oxide.

11.36 The Rarer Metals in Glass.

Anon

Vancoram Review, vol. 1, no. 5, pp. 149-152, Oct. 1930

The presence of vanadium in glass tends to make it absorb ultraviolet light. A particular application of this property is in nonshatterable glass, as ordinary glass permits deterioration of the celluloid cementing material. Nickel vanadate produces shades of yellow green to deep violet, manganese vanadate gives yellow green to amber to wine red, cobalt vanadate gives green to blue and copper vanadate gives yellow green to blue green. The shades depend upon the type of glass and on furnace conditions.

11.37 Ceramic Products.

Singer, F.

Fr. 645,726. C. A. 23, 2006 (April 20, 1929). Vancoram Review. vol. 1, no. 2, p. 62 (Jan. 1930)

To prevent the aging of ceramic products, compounds (Particularly the oxides) of Ce, Zr, Cr, Mn, P, W or V are added to the usual constituents.

11.38 Color Given to Glass by Vanadium.

Fuwa, Kitauzo

J. of Japanese Ceram. Assoc, vol. 369, p. 236-240. See J. Soc. Glass Tech., vol. 28, 1944, pp. 187-8

The influence of the composition of glass on the color imparted by V205 was determined. In general, the color resembles that given by Cr203, and it is not influenced by the composition of the glass. An oxidizing agent causes a slight increase in yellow. The color of vanadium glass may be due chiefly to V203 which may be partially oxidized to V20.-, which may be a yellow colorant in glass.

B. Opacifiers.

11.39 V20- — Opacified White Enamels.

Smailey, A. K.; King, B. W.; Duckworth, W. H.

J. Am. Ceram. Soc, Aug. 1, 1957, pp. 253-255

Whiteness and opacity developed by addition of 3 to 8 percent V205 to lead borosilicate enamels on glass and aluminum is discussed.

11.40 Vanadate Glasses.

Denton, E. P.; Rawson, H.; Stanworth, J. E.

Nature, May 29, 1954, vol. 173, no. 4413, pp. 1030-32. Ceram. Abs. 1955, 1781

Work on V?Or, tellurite glasses indicates that secondary glass-iorming oxides as phosphorus pentoxide and others can be used to make opaque glasses.

11.41 Recent Glaze and Color Developments (Vanadium-Zirconium Yellows).
Bui. Am. Ceramic Soc, 1952, vol. 31, pp. 161-64.

Zirconium-vanadium stain will increase the opacification. Low calcium base frit produces most favorable base for Zr-V yellows and recently produced at Eastern tile plant firing at cone 1.

11.42 Colored Glasses Pt. 5; Fluorescence and Solarization of Glass.
Weyl, W. A.
J. Soc. Glass Tech.. vol. 30, 1946, p. 139

Some crystalline modifications of vanadates exhibit yellow fluorescence. Zinc vanadate is outstanding in its intensity. Pentavalent vanadium is the carrier of fluorescence.

11.43 Yellow Fluorescent Material and Making the Same.
Weyl. W. A.
U. S. Pat. 2,322,265 — June 22, 1943

Crystalline modifications of vanadates exhibit yellow fluorescence in glasses are discussed.

11.41 Title Unknown.
Robl. R.
Z. Angeu. Chem., vol. 39, 1926, p. 608-611

Some vanadates possess a weak brownish fluorescence. (See J. Soc. Glass Tech., vol. 28, no. 128, 1944, p. 189).

C. Additives Abetting Glassy Phase Formation.

11.45 Semiconducting Properties of Some Vanadate Glasses.
Baynton, P. L.; Rawson, H.; Stanworth, J. E.
J. Electrochem. Soc, vol. 104, no. 4, 1957, pp. 237-40

Glasses have been made in systems BaO-V2O.,-P2O0 and Na2O-BaO-V2O-,-P2Or) with V2O;; contents ranging between 50 and 87 mole percent. All the glasses were very intensely colored and appeared black in any thickness other than that of very thin films, the color of these films being dark green.

11.46 Glass Refractory Composition.
U. S. Pat. 2,748,007. Issued May 29, 1956.
Badger, Alfred E. and Sharp, Donald E.

A glass contact refractory consisting essentially of from 30 to 45 percent aluminum oxide, 50 to 70 percent silicon oxide. and from 1 to 5 percent of an oxide of a metal selected from the group consisting of chromium and vanadium is reported.

11.47 Vanadate Glasses.
Denton, E. P.; Rawson, H.; Stanworth, J. E.
Nature, 1954, vol. 173, no. 4413, p. 1030+

Prepn. and properties of a number of glasses based on vanadium pentoxide V2O5-P2O5 system glasses contained as much as 90 percent V2OB are discussed.

11.48 Use of Rare Oxides for Glass Coloring and Decoloring.

Herfurth, R.
Glas-Email-Keramo-Technik, 1952, vol. 3, no. 1 and 2, pp. 1-4, 38-40

The necessity of basic research in this field of glass chemistry and of careful studies by glass technologists before using rare earths as decoloring agents is evident.

11.49 Studies of Some Special Glasses Absorbing Ultraviolet Rays and Transmitting Visible Light.

Ctyroky, V.
Sklarskerozhledy, vol. 23, 1947, pp. 97-114. Refer Ceram. Absts. 1948, p. 33

Cerium and vanadium absorb ultraviolet rays best but are somewhat greenish. Preferred combinations were 1.9 to 6.5 Ce20:! with 0.5 to 2 percent V20.-.

11.50 Color and Solarization of Classes Containing Combinations of Coloring Oxides.

Gagin, L. V.; Bachman, G. S.; Badger, A. E.
Glass Ind., vol. 27, 1946, pp. 500-1; 530-1

Chromium oxidizes manganese but antimony arsenic, iron. copper and vanadium reduce it. Antimony vanadium, copper, cerium reduce hexavalent chromium to the green trivalent form.

11.51 Colored Glass Fibers.

Schoenlaub, R. A. (Owens-Corning Fiberglas Corp.)
U. S. Pat. 2,394,493 — Feb. 5, 1946

A vitreous composition of matter suitable in the production of colored fibers by an attenuating process comprising an alkali-free glass containing 10 to 20 percent vanadium oxide V203. Colors obtained were henna, brown, mahogany and black.

11.52 Some Observations on Solarization and Regeneration.

Weyl, W. A.
J. Soc. Glass Tech.. vol. 30, no. 138, 1946, pp. 163-4.

Ce203 + V203 = 2Ce02 + 2VO reaction taking place in cerium and vanadium containing glasses, producing a striking change from green to purple is described.

11.53 Leadless and coloured Fitted Glazes.

Parmeloe, C. W.
Deram. Ind., vol. 45, 1945, Nov., pp. 84-88

Sodium uranate would produce yellow colors in glazes containing a high content of sodium and barium.

D. Color Stabilizers for sewer pipe glazes.

11.54 Vanadium-Molybdenum Staining on Building Products.

Stahmann, John A.
Bulletin Am. Ceram. Soc, 1955, vol. 34, pp. 138-144

Review of causes of effluorescence describing testing methods Detailed 4 page bibliography included.

11.55 Red Glazes with Uranium.

Jaeschke, A.

Keram. Z., 1949, vol. 1, p. 57+

To produce V good red with U;!0S, it was found that the glaze should be basic mainly PbO. Other bases turn the glaze brown or yellow. (Brit. Ceram. Abst. 49. no. 6, 1950, p. 230a).

11.56 The Occurrence of Vanadium in Ceramic Raw Materials and Ware and Its Effect Upon the Fusibility as Well as the Color and Formation of Scum on a Pure Kaolin and a Brick Clay.

Kallauner, 0. and Hruda, L.

Sprechsaal, 45, 333-5, 345-9 (1922). C. A. 17. 862

A large number of minerals contain V in small amounts, and among these is clay. Seger pointed out that KV03 often causes a scumming and yellow discoloration on brick clays. A study was made of the effect of V20- on fusion, discoloration and scumming. V20-, in small amounts does not affect the fusibility of kaolin but in larger amounts acts as a strong flux as is shown below:

Kaolin	100	99	95	90	80	60	40	20	0%
V.O-,	0	1	5	10	20	40	60	80	100%
Fusion cone ..	35	34	33	32	30	15	5a	08a	675°

The V2On causes a yellow discoloration when present in quantities as low as 0.1 percent. This discoloration may be partly reduced bv firing with a reducing kiln atm. and by the addition of Ba or Ca compounds as is shown below. All tests were made on a mixture of 99 percent kaolin and 1 percent V20-, and the amount (in mg.) of solution V20.-, after the different treatments was used to compare the different methods.

E. Constituent in porcelain enamel.

11.57 Effects of Vanadium Oxide on the Adherence of Heat-Resisting Enamel Applied on Nickel-Chrome Stainless Steel.

Tashiro, Hegumi; Sakka, Sumid; Teranishi, Hironori

J. Ceram. Assoc. Japan, 1953, vol. 61, no. 689, pp. 537-40

By a mill addition of 2 to 10 parts V20.^ to 100 parts enamel frit the adherence of the enamel was increased.

11.58 Title Unknown.

Every, Cecil E. (Titanium Alloy Mfg.)

Brit. Pat. 590,583, July 22, 1947

A ceramic electrical-resistance body with major ingredients Ti02 and V203 or several other oxides is described. Molecular proportions of TiOo to other oxides should not be greater than 20:1.

F. General reference.

11.59 Symposium on Developments in Applied Chemistry. Some Scientific and Technical Developments in Glass Technology and Ceramics During the Last Quarter Century.

Weyl, W. A.

Pennsylvania State College, 1951

Twenty-three references are included.

11.60 Glass — A Handbook for Students and Technicians.
Dickson, J. Howe, editor
Chemical Publishing Company, publisher — 1951
Colors given by various oxides are noted.

Section 12.00 — General Information and History

12.01 Extractive Metallurgy of Vanadium.
Burwell, B.
J. of Metals, v.d. 13, no. 8. Aug. 1961, pp. 562-566

12.02 Vanadium.
Mining Journal, Annual Review 1961, pp. 41
A summary of the current and potential uses of vanadium is given.

12.03 Mineral Facts and Problems (Vanadium Section).
Busch, P. M.
U. S. B. M., Bull. 585, 1960
A summary of the occurrence, production, and uses of vanadium is given.

12.04 Report of the Raw Materials Group, Panel in Vanadium, National Academy of Sciences — National Research Council, Report MAB-154-M91), vol. II, Panel Reports, chap. 8, sec. A,1 pp. 228-247, Oct. 1959

12.05 Atomic Age Metal Extraction.
Coffer, L. W.
Chem. Eng., vol. 65, no. 2, Jan. 27, 1958, pp. 107-122

12.06 If You're Planning Uranium Extraction, Take a Look at Today's Flowsheets.
Lenneman, W. L.
Eng. & M. J., Mining Guide Book, Mid June 1956

12.07 Finland.
Min. World, vol. 18, no. 5, April 1956, pp. 121
The Otanmaki operation is reviewed.

12.08 History and Trends of Uranium Plant Flowsheet.
Lundquist and Lake
Min. Cong. J., vol. 41, Nov. 1955
A history of uranium (and vanadium) production on the Colorado Plateau is discussed.

12.09 Making Uranium at Monticello.
Philippone, R. L.
Chem. Eng. Prog., vol. 51, June 1955, pp. 261-265
The various procedures used at the Monticello (Utah) mill for processing of ores containing uranium and vanadium is discussed.

12.10 Process Development Studies for Lukachukai Ores
McLean, D. C.
ACCO-65, April 1955

12.11 Rare Metals Handbook — Vanadium Chap. 32
Dunn, Edlund, Griffin
Reinhold Pub. Co., 2nd ed, 1961
C. A. Hampel. Editor

12.12 Materials for the Chemical and Allied Industries
Johnstone, S. J.
J. Wiley & Sons, 1954
A chapter on the vanadium industry is included.

12.13 Proposed Flowsheet for Recovery of Uranium and Vanadium from Temple Mt. Ores.
Ehrleinger and Stephens
AECD-3725, 1953

12.14 Vanadium.
Iron Age, vol. 170, no. 14, Oct. 9, 1952, pp. 285
This is a short article on vanadium and vanadium metal.

12.15 Iron-Titanium Mine Starts Up in Finland.
Stigzelius, H.
Eng. & Min. J., vol. 153, no. 5, May 1952, pp. 126-127
The development of the Otanmaki operation is discussed.

12.16 Vandium.
Vivian, C. H.
Compressed Air Mag., vol. 50, no. 10, Oct. 1945, pp. 260-264
A brief historical review of the operations of the Rifle Mine and plant is presented.

12.17 Vanadium Operations at Monticello, Utah.
Min. World, vol. 6, no. 3, March 1944, pp. 17-21
The article gives a description of construction and operation of the vanadium mill at Monticello, Utah, (1942-1944).

12.18 Mina Ragra: A Historical Report on the Discovery and Development of the World's Greatest Single Source of Vanadium.
Vancoram Review, vol. 4, no. 4, 1945, pp. 3-6

12.19 Naturita — Then and Now.
Kent, F. F.
Vancoram Rev., vol. 4, no. 2, 1945, pp. 3-5

12.20 Vanadium Sources and Beneficiation.
McLaren, D. C.
Min. Mag (Lond), vol. 71, 1944, pp. 203-212

12.21 War Plant from Scrap Pile.
Min. World, vol. 6, no. 4, April 1944, pp. 14-16
The construction of the Durango, Colorado, vanadium plant in 1942 is discussed.

12.22 The Occurrence and Production of Vanadium.
Argall, G. 0., Jr.
Quarterly of the Colo. School of Mines, vol. 38, no. 4, Oct. 1943

12.23 Smelting of Vanadium Bearing Titaniferous Sinter in an Experimental Blast Furnace.
Wood, Joseph and Cole
U.S.B.M. RI 3679, 1943

12.24 Vanadium.
Hess, F. L.
U.S.B.M. IC-6572, 1932

12.25 Vanadium in Iron Ores and Its Extraction.
Von Seth, R.
Eng. & Min. J., vol. 120, no. 2, July 1925, pp. 51-56

12.26 Radium, Uranium, and Vanadium Deposits of South Western Colo.
Colo. State Geol. Survey Bull. 16, 1921

12.27 Extraction and Recovery of Radium, Uranium, and Vanadium from Carnotite.
Parsons, Moore, Lind, Schaefer
U.S.B.M. Bull. 104, 1915

12.28 A Preliminary Report on Uranium, Radium, and Vanadium.
Moore and Kithel
U.S.B.M. Bull. 70, 1913

12.29 Process for Treating Complex Radium Ores.
Radcliff, L.
U. S. Pat. 1,049,145, 1912
A sodium sulfate fusion method is discussed.

12.30 Vanadium.
Colo. State Bureau of Mines, Bien. Report, 1909-1910

12.31 Vanadium and Uranium.
Colo. State Bureau of Mines, Bien. Report, 1907-1908

12.32 A Study of the Uranium and Vanadium Belts of Southern Colorado.
Fleck, Herman, and Haldane
Colo. State Bur. of Mines, Bien Report, 1905-1906

12.33 The Discovery of Carnotite.
Kimball, G.
Eng. & Min. J., vol. 77, 1904, pp. 956