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VANADIUM

BY P. E. JOSEPH

INTRODUCTION

Vanadium was first discovered in 1830 by a Swedish chemist, Sefstrom, in a specimen of iron from the ores at Taberg, Sweden. The pure metal is light, grayish-white in color, having a silver white luster. It is not affected by air or water at ordinary temperatures; does not volatilize at a strong red heat; is fusible with difficulty, but burns brilliantly when heated in air or oxygen or thrown in powder form into a flame.

ORES OF VANADIUM

Most of the vanadium produced in this country up to the present time comes from roscoelite, carnotite and patronite, but vanadinite and descloizite are also important minerals of vanadium.

Roscoelite—Most important ore of vanadium.
Composition—Vanadium-aluminum-silicate, containing 28.85 per cent of $\text{V}_2\text{O}_5$.

General Description:—A soft, pearly mineral, occurring in minute scales and often in fan-shaped groups. It has a micaceous structure, perfect cleavage, and varies in color from dark clove-brown to greenish-brown and dark brownish-green.

Physical Characteristics:—
- Hardness (1-2) very soft.
- Sp. Gr. (2.92) light.
- Lustre, pearly.
- Translucent.
- Streak, greenish-brown.
- Cleavable.
- Color, dark clove-brown, greenish-brown, dark brownish-green.

Qualitative Tests:—If heated in the blowpipe flame it fuses to a black. With salt of phosphorous it gives a dark yellow bead in the oxidizing flame, which assumes an emerald green color in the reducing flame.

Occurrence:—In Magnolia district, Colorado; at Granite Creek, Eldorado County, California; in association with carnotite, it occurs in the Placerville district, San Miguel and Montrose counties, Colorado.
CARNOTITE

Composition:—Uramil potassium vanadate. However, it never occurs pure, but always contaminated with calcium and barium compounds, and a mixture of silicates containing vanadium, thus increasing the vanadium content of the mineral.

General Description:—A very soft, ochrous, canary-yellow mineral, which leaves traces whenever touched or placed.

Qualitative Tests:—With borax it colors beads yellow when hot, colorless cold in the oxidizing flame, and green in the reducing flame. Ammonium sulphide, (NH₄)₂S, precipitates black uranous sulphide. Ammonium or potassium, or sodium hydroxide will precipitate red-brown gelatinous hydrate, while the carbonate of the above will throw down green uranous hydrate, which is soluble if the salts, especially ammonium carbonate, are added in excess.

Occurrence:—In Montrose, San Miguel, Dolores and Montezuma counties, Colorado. Also in Utah in small quantities.

VANADINITE

Composition:—(3Pb₈(VO₄)₂PbCl₂). It is a mixture of lead vanadate and lead chloride, and when pure contains 19.4 per cent of V₂O₅. Often phosphorus and arsenic replace vanadium.

General Description:—A bright red to yellow-brown mineral, occurring usually in sharp hexagonal prism. Also in parallel groups and globular masses of crystals.

Physical Characteristic:

Hardness, (3) easily scratched by knife.

Lustre, resinous on fracture.

Streak, white to pale yellow.

Color, deep red, bright red, yellow or brown.

Qualitative Tests:—Fuses easily on charcoal to a black mass yielding a yellow sublimate in the reducing flame. The residue gives a deep green bead, with salt of phosphorus in the reducing flame. When the powdered mineral is treated with strong nitric acid it first becomes deep red and finally dissolves to a yellow solution. When the powdered mineral is treated with KHSO₄ it yields a clear yellow, then a red product, which finally becomes yellow when cold.

DESCLOIZITE

Composition:—(Pb Zn) (PbO H) VO₄. When pure contains 22.7 per cent V₂O₅.
General Description:—Small purplish-red, brown or black crystals, forming a drusy surface or crust. Also fibrous and less frequently massive.

Physical Characteristics:—
Hardness (3.5) easily scratched by knife.
Lustre, greasy.
Streak, orange or brown.
Color, purplish red, brown, or black.

Qualitative Tests:—On charcoal fuses to black mass, enclosing metal.
In closed tube yields water, which is collected in globules on sides of tube. Vanadium reaction as in vanadinite.

PATRONITE

Vanadium sulphide, containing 15 per cent vanadium. Patronite, important although not of common occurrence in the United States, is a very important source of vanadium, and is chiefly mined at Minas Ragra, near Cerro de Pasco in Peru, owned the the American Vanadium Company of Pittsburg, who claim that 90 per cent of the world’s supply of vanadium comes from Peru.

Other minerals of vanadium are:
Endlichite, which is composed of vanadinite and mimetite (lead arsenate) in the proportion of 1 molecule of mimetite and 1 molecule of vanadium. 1 molecule of endlichite. Its chemical composition is represented by the formula Ph5Cl (AsO₄)₃ Pb₅Cl VO₄)₃.
Hewettite:—CaO 3V₂O₅ 9H₂O. This mineral is of a mahogany red color with silky to earthy lustre. It is found in Peruvian ores and is probably an oxidation product of patronite with partial replacement of vanadium by calcium.
Pascoite:—Ca₂VO 11H₂O. Red-orange mineral of sub-adamantine lustre, occurring in thin, probably mono-clinic plates. Found in the Peruvian ores and, as Hewettite, is probably derived from patronite by oxidation and shows further replacement of vanadium by calcium.
These minerals, however, are of little, if any commercial importance.

METALLURGY OF VANADIUM

The extraction of vanadium from its ores involves considerable difficulty. A good many methods have been patented and invented,
such as involve smelting, fusion, hydrometallurgy, electro-chemistry. Of these, the method of extracting vanadium by electro-chemical and hydrometallurgical means has been most economical. The greatest difficulty in treating the ore by these methods is to economically get the vanadium in solution free from gangue.

The chief method of extraction is by leaching with mineral acids and by alkalies.

Patronite is treated first by roasting to reduce to oxide and then decomposing it with sulphuric acid.

Roscoelite is treated with a mixture of 1:1 mixture of sodium chloride and crude lye, the ore being roasted and then leached with water.

Vanadinite is treated with sulphuric acid which decomposes it to a certain degree.

Carnotite, which is one of the principal ores of vanadium in the United States, is treated in the following ways:

1. By the action of hydrogen chloride gas it has been shown that in time the vanadium is completely removed, leaving a residue consisting of sodium uranite, sodium chloride, uranyl chloride, and the other impurities in the crude uranate.

   The uranium may be removed from the residue by either of two methods: (1) By boiling with excess of ammonium chloride, which converts the uranium into ammonium uranate, which may be ignited to uranium oxide. (2) By dissolving the residue in a dilute mineral acid and precipitating the uranium with ammonia, as ammonium uranate, which may be converted into uranium oxide by ignition.

   The percentage recovery of uranium oxide, free from vanadium, but containing a small percentage of iron, which is not objectionable for its sale, varies from 59 to 64 per cent.

2. By mixing the vanadium bearing uranate with twice its weight of ammonium chloride and enough water to make a thick paste, the vanadium may be nearly completely volatilized by heating in a porcelain crucible. When subjected to proper conditions of temperature, it is possible to reduce the quantity of vanadium present in the crude uranite from 8.5 per cent to less than one-half of 1 per cent. The ammonium chloride serves the double purpose of converting a part of the uranium present to ammonium uranate, which, upon ignition, yields uranium oxide as well as removing the vanadium.

   The percentage of uranium recovered may be regulated very materially by the heat treatment to which the mixture is subjected, where the residue, after volatilization of the ammonium chloride, is heated to a high temperature, the percentage recovery of the uranium oxide
(U₃O₈) is reduced due to the fact that some of the uranium oxide formed in the operation is converted back to sodium uranate.

The highest percentage recovery was obtained where the temperature was not raised any higher than necessary to volatilize the ammonium chloride and vanadium compounds.

In this connection it was found that a mixture of fifteen grams of ammonium chloride and five grams of ammonium nitrate to every ten grams of crude uranate served the purpose of removing the vanadium from the crude uranate just as well as the ammonium chloride alone. However, the percentage recovery of uranium oxide is reduced very materially, as it is only possible to get a recovery of about 58 per cent under the most favorable conditions of temperature. This reduction in the percentage of recovery more than counterbalances any advantage that the use of ammonium nitrate might have as a partial substitute for ammonium chloride.

3. The vanadium can be completely precipitated by dissolving the crude uranate in the least possible amount of dilute nitric, hydrochloric and some times sulphuric acid, and then boiling the solution. Approximately 13 per cent of the uranium is precipitated out with the vanadium, but the amount is small compared to that which remains in solution. The uranium may be recovered by adding ammonia to the solution containing the uranium, free from vanadium, to precipitate it as ammonium uranatem, which may be converted into uranium oxide by ignition.

The percentage recovery of uranium oxide in the case of nitric and hydrochloric acid treatments is found to vary from 58 to 79 per cent. Some uranium is lost in the dilute sulphuric acid treatment of the residue for the removal of the sodium uranate, but this uranium may be recovered from the acid solution by precipitating with ammonia.

Only by one of the above methods is the removal of vanadium and the conversion of the uranium oxide accomplished in one step. That is the case of the ammonium chloride treatment. In all of the other processes the vanadium is removed by one step and the uranium recovered by another operation. However, it will be noted that the percentage of recovery of uranium oxide by all the methods was practically the same.

4. Probably hydrogen chloride (gas) may also be utilized to remove the vanadium from carnotite ores quantitatively, by proper regulation of temperature.
VANADIUM IN THE UNITED STATES

The great importance of vanadium in the steel industry, manufactures and the arts has stimulated the search for deposits of vanadiferous ores of commercial value. While the occurrence of vanadium is widespread and varies, it is rarely found in such quantities as to be profitably worked.

Vanadium ores are found in a number of states, as in Arizona, Colorado, Michigan, New Mexico and Utah.

**Arizona:** Vanadium is found at numerous places. As vanadinite it occurs in association with lead ores—in Cochise County, near Fairbanks. Gila County, Globe district, at Lockwood claim and Clara and Stewart claims near the Old Dominion mine. Pima County, Old Yuma mine, 14 miles northwest of Tucson. Pinal County, Mammoth mine at Schultz; Royal Dane claim, 7 miles southwest of Oracle; Black Prince mine, Pioneer district, and at Kelvin. Yavapai County, near Silverbell mine, Big Bug district. Yuma County, Red Cloud mine.

Descloizite is found in Cochise County, Lucky Cuss mine, Tombstone, Castle Dome district. Mammoth mine in Catalina Mountains and Old Yuma mine in Tucson Mountains. Bully Cave mine in Cave Creek district, Maricopa County, and in the Dripping Springs Range, 4 miles east of Kelvin, Pinal County.

Carnotite is reported to have been discovered in the Navajo Reservation. It has been found in commercial quantities in the Vanadinite group of claims, 3 miles north of Globe.

No production of vanadium has ever been reported from this state.

**Colorado:** This state has been the chief producer of vanadium in the United States. The deposits are located near Placerville, San Miguel County, southwestern Colorado, at the western base of the Rocky Mountains. Although the percentage content of vanadium in the ore is low, the deposits are of commercial value due to the scarcity of sources from which vanadium can be obtained profitably. These deposits are best described by F. L. Hess in U. S. Geological Bull. 530. 1911.

**New Mexico:** Grant County, vanadinite with silver ores at Mimbres and McGregor mines; also found on Red Horse and White Horn claims, Georgetown district; mined at Lucky Bill mine, Bayard Station. Sierra County, it has been mined in Caballos Mountains and with lead in the Hillsboro district; also in Bella, Apache, and Grande mines, Lake Valley district. Socorro County, mined at Kelly mine and found on other claims in the Magdalena district.

Descloizite is found at the Commercial mine, Georgetown, Grant
County. Endlichite is found at Hillsboro and in Lake Valley district, Sierra County.

**Utah:** Calcium vanadate has been mined in a small way with carnotite in asphaltic sandstone in Wild Horse Canyon, Emery County; also on claims 8 miles south of Thompson's and 20 miles south of Cisco, in Grand County. Carnotite is also found in a number of localities, but is only mined in Emery County on the east flank of San Rafael swell, 18 miles west of Green River, and in Grand County, near Richardson, where it occurs in sandstone with chalcivilborthite and copper minerals.

### VANADIUM IN FOREIGN COUNTRIES

The largest producer of vanadium is the American Vanadium Co. of Pittsburg, Pa., whose mines are in Peru. The mines of this company are said to have an almost inexhaustible supply of patronite, and are located at Minas Ragra, 23 miles northwest of Cerro de Pasco.

The production of vanadium for commercial purposes is confined entirely to the United States, Spain and Peru, although it is found sparingly in Mexico, France, Portugal and England.

### USES OF VANADIUM

The most important use of vanadium is in the manufacture of steel, where it is introduced in the form of an iron alloy. The addition of a very small amount of vanadium increases essentially the malleability and hardness of steel after tempering. This affords a ready means for producing sheet steel and armor plates, possessing a very hard surface, but a soft interior.

Vanadates and hypo-vanadates are used in the printing of calico and in fixing aniline black on silken fabric, and in the preparation of an indelible ink.

The oxides of vanadium are used in the decoration of porcelain and pottery.

### MARKET AND PRICES

The market demand for vanadium has increased considerably and while there are no statistics on hand, it is fair to assume an increased output over the preceding year.

The basis of settlement for vanadiferous ore varies greatly in different districts and with different companies. A very satisfactory quo-
tation by one of the European buyers is: Ore containing a minimum content of 10 per cent vanadic acid command an average price of 50 cents per pound $V_2O_5$ contained, F. O. B. cars shipping point. The price of ferri-vanadate has varied from $3 to $5 per pound.