



Vanadium, the new green metal: Mineral deposits in the Colorado Plateau

by A.D. Hammond

Vanadium is a transition metal, ductile and silver-gray. It is harder than most metals and steels and it has a good resistance to corrosion. It is stable against alkalis and sulfuric and hydrochloric acids. Vanadium is oxidized in air at

vanadium production comes from the processing of petroleum residues, fly ash and recycling spent catalysts.

In 2011, metallurgical applications accounted for 93 percent of the use of vanadium. Here, an alloy called ferrovanadium is used to strengthen steel to be used as rebar in the construction industry, in the manufacturing of axles, crankshafts, gears and chassis in the automotive and transportation industries and in the manufacturing of high-speed tools. In the aerospace industry, vanadium is used as a titanium alloy in the manufacturing of airframes and jet engines. The reason for the wide use of vanadium as alloy is its high strength-to-weight ratio, the highest of any engineered material on earth.

The major nonmetallurgical use of vanadium is in the production of catalysts for the chemical industry. The most commercially important compound is vanadium pentoxide (V_2O_5), which is used as a catalyst in the production of sulfuric acid.

Vanadium statistics

In 2011, the world mine production of vanadium amounted to 61.2 kt (67,400 st). The major producers are China, South Africa and Russia, accounting for 98 percent of the world production. In the United States, there are no primary vanadium mines. The vanadium produced in mining totaled 590 t (652 st) of vanadium pentoxide (V_2O_5) and came as a byproduct of uranium at the White Mesa uranium mine in Utah.

In 2011, the United States consumed 5,120 t (5,643 st) of vanadium, mostly as ferrovanadium. The United States imported 80 percent of the vanadium consumed. The ferrovanadium was imported from Korea, Canada and Austria. The vanadium imported in the form of vanadium pentoxide came from Russia, South Africa and China. Collectively, the import of vanadium in the United States is valued at \$13.8 million. From the supply/demand perspective, the vanadium market is considered to be in balance.

In 2011, the average domestic price of ferrovanadium was \$14.80/lb of vanadium content. For the vanadium pentoxide, the average price was \$6.50/lb.

The U.S. government does not have stockpiles of vanadium in any of its chemical derivations.

The world reserves of vanadium is estimated to be 14 Mt (15.4 million st), with China, Russia



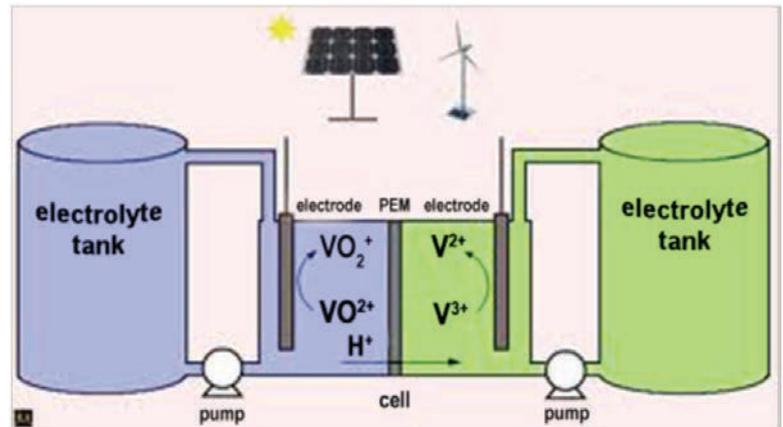
Perspective view of the inner (concave) surface of a mined roll at the Cougar Mine. This view shows the form of a typical C-shaped roll.

about 660° C (1,220° F), although an oxide layer forms even at room temperature. The chemistry of vanadium is noteworthy for the accessibility of the four adjacent oxidation states, 2-5. In aqueous solution, the colors are lilac V^{2+} , green V^{3+} , blue VO^{2+} and, at high pH, yellow VO_4^{2-} .

Considered to be as abundant as zinc, metallic vanadium is not found in nature, but it is known to exist in about 65 different minerals. Economically significant examples include patronite (VS_4), vanadinite ($Pb_5(VO_4)3Cl$), associated to the uranium mineral carnotite ($K_2(UO_2)_2(VO_4)2 \cdot 3H_2O$) and in a vanadium mica called roscoelite $K(V^{3+}, Al, Mg)[(Si, Al)_4O_{10}(OH)_2]$. Other important vanadium ore oxides are montroseite $(V, Fe)O(OH)$ and corvusite $(Na, Ca, K)V_8O_{24} \cdot 4H_2O$. Much of the world's vanadium mine production comes from magnetite-hosted deposits and, to a lesser extent, sedimentary-hosted sandstone.

Vanadium is also present in bauxite and fossil fuel deposits such as crude oil, coal, oil shale and tar sands. In crude oil, concentrations up to 1,200 ppm have been reported. Significant

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Figure 1
Schematic of the vanadium redox battery.

Advantages of the vanadium redox battery.

The advantages of the vanadium redox batteries relative to lithium, cobalt and lead acid batteries include:

- Scalability: the capacity of the battery can be increased by simply using larger storage tanks or stacking more cells in series or parallel.
- The battery is easily recharged by replacing the electrolyte if no power source is available to charge it.
- The battery can be fully discharged without harming it.
- There is no cross-contamination, as there is only one element in the electrolyte.
- The solution has indefinite life and can be recycled, thus eliminating the waste disposal problem.
- Can be recharged at high rates at a fraction of the time needed for the lead acid battery.

Applications of the vanadium redox battery.

The extremely large capacities possible from vanadium redox batteries make them well-suited to use in large power storage applications such as helping to average out the production of highly variable generation sources such as wind or solar power, or to help generators cope with large surges in demand.

The limited self-discharge characteristics of vanadium redox batteries make them useful in applications where the batteries must be stored for long periods of time with little maintenance while maintaining a ready state. This has led to their adoption in some military electronics, such as the sensor components of the GATOR mine system.

Their extremely rapid response times also make them superbly well-suited to the uninterruptable power supply (UPS) type of

and South Africa accounting for 97 percent of the world reserves.

In the United States, American Vanadium Corp. reports that its 100-percent controlled Gibellini project in Nevada contains 59,588 million kg of vanadium pentoxide in measured and indicated resources at a grade of 0.285 percent. The company estimates an annual production of 5,170 t (5,698 st) of vanadium pentoxide from its openpit heap leaching operations by 2013 or 2014.

New uses of vanadium in green technologies

The need for clean and renewable sources of energy is generating increased interest in vanadium due to the recent development of the vanadium flow battery, also known as vanadium redox battery (VRB), and its utilization in the storage of energy produced by green sources such as wind and solar. One of the major problems of renewable energy sources is its inherently intermittent supply. The vanadium flow batteries allow the intermittent energy supplies to be stored and regulated into what the electricity industry refers to as “dispatchable energy,” which enables the grid to balance the amount of energy and provide a continuous flow to consumers.

Vanadium redox batteries

The concept of the vanadium redox battery was originally developed by NASA in the early 1970s and commercially developed and patented by the University of New South Wales in Australia in the 1980s.

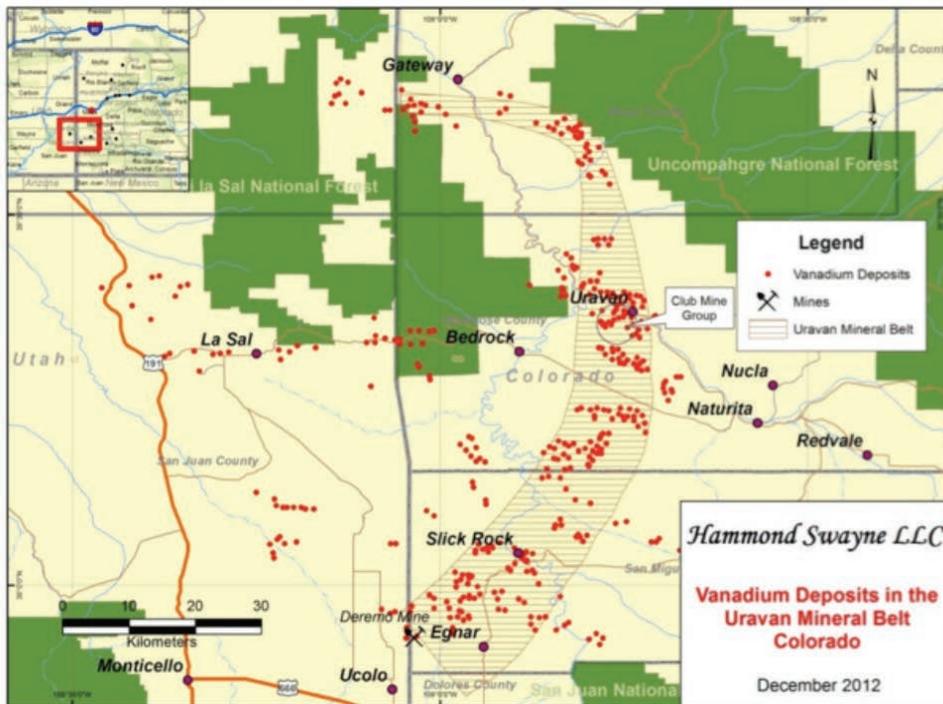
The vanadium redox battery is a type of flow battery with two half-cells containing vanadium in a sulfuric acid solution. The vanadium redox battery exploits the ability of vanadium to exist in solution in four different oxidation states, and uses this property to make a battery that has just one electroactive element instead of two. Each half-cell is composed of a vanadium redox couple. At the anode, VO^{2+} ions are converted to VO_2^+ ions when electrons are removed from the positive terminal of the battery. At the cathode, electrons convert V^{3+} ions into V^{2+} ions when electrons are introduced to the negative terminal of the battery. This occurs when the battery is charged. During discharge, this process is reversed and results in a typical open-circuit voltage of 1.41 V at 25° C (77° F). The electrolytes of the two half-cells are separated by a proton exchange membrane (Fig. 1).

In the vanadium redox battery, the half-cells are connected to storage tanks and pumps, allowing large volumes of the electrolytes to circulate. This results in high capacity batteries, making them ideally suited for large-scale power storage.



Figure 2

Uraivan Mineral Belt in Colorado and Utah.



Jurassic and Cretaceous rocks in the Yauli region of Pasco. The deposit is emplaced entirely within a red shale strata that was intensely faulted, altered and intruded by dykes of diverse composition. Patronite, a vanadium sulfide, permeates the porous country rock and is the mineral with the greatest economic value, assaying up to 25 percent vanadium.

News of the discovery of Minas Ragra reached Joseph M. Flannery, a bolt manufacturer in Pennsylvania, who immediately dispatched two geologists to Peru to confirm the quality of the deposit and conduct negotiations for the purchase of the mine from the owner, Eulogio Fernandini. Being short of funds, Flannery offered Fernandini \$10,000 in cash and 10 percent in stock of the newly formed company, the American Vanadium Co.

application, where they can be used to replace lead-acid batteries and even diesel generators.

Current installations of the vanadium redox battery are spread around the world. Most notably, they are in a wind power project in the Tomari Wind Hills of Hokkaido, an electric storage system in the remote area of Castle Valley in Australia, and as an output balancer in use on a solar power project in the Bilacenge Village in Sumba Island, Indonesia.

Vanadium-lithium phosphate battery

The vanadium-lithium phosphate battery is a type of rechargeable battery commonly found in consumer electronics such as laptop computers and cell phones. Its use has been extended to the automotive industry in the development of electric vehicles.

The main advantages of these types of batteries are improved safety and greater power, up to 20 percent more storage power than the lithium-cobalt battery.

Recent research at Subaru and Nissan Motors indicates that the vanadium-lithium phosphate battery doubles the driving range to 200 km (124 miles) and can be recharged in 10 minutes.

Famous vanadium deposits

Located in the central Peruvian Andes, Minas Ragra was discovered in 1905. The deposit lies along the western limb of a broad anticline in

In 1907, Minas Ragra produced 201 t (234 st) of vanadium, mostly dug by hand and hauled on the back of llamas but, with the increasing demand for vanadium from the United States, production quickly ramped up, and by 1919, it produced 1.1 Mt (1.2 million st). The high grade from this mine ran as high as 40 percent V₂O₅ and, for years, Minas Ragra produced half of the vanadium consumed in the world.

Production of V₂O₅ reached 2,073 t (2,285 st) in 1941, when 971 t (1,070 st) were shipped to the United States, comprising 100 percent of all imports of vanadium into the United States. Lower grades continued to be mined until 1955, when the orebody was mined out. The mine was abandoned in 1959.

Minas Ragra played a transformational role in the steel and automobile industries in North America, as it made possible the production of steel and cars at competitive prices. Essentially, the production from Minas Ragra caused the price of vanadium to drop from \$4,792/lb to as low as \$5.50/lb. The use of the vanadium alloy represented significant cost savings as it reduced the amount of steel required for the chassis, axles, gear, crankshafts and springs.

Vanadium deposits in the Colorado Plateau

The first recorded production of vanadium in the United States dates back to 1910.

By 1941, the United States became the largest

Figure 3
 Roll surfaces and vanadium concentration (after Shawe).

producer of vanadium in the world. Because of the imminent war in Europe and in the Pacific, the U.S. government created the Metals Reserve Co. and declared vanadium a strategic resource.

The principal vanadium ore district in the United States has been in southwestern Colorado and southeastern Utah. The vanadium resources are large, but the individual orebodies are widely scattered and generally small. Although the percentage of vanadium in the ore is relatively low, the deposits were of commercial value due to the scarcity of sources from which vanadium can be obtained profitably. Historically, the most important vanadium deposits are located in the Uravan Mineral Belt on the Colorado-Utah border, the Placerville deposits in San Miguel County and the Rifle Creek deposits in Garfield County, both in Colorado.

Uravan Mineral Belt

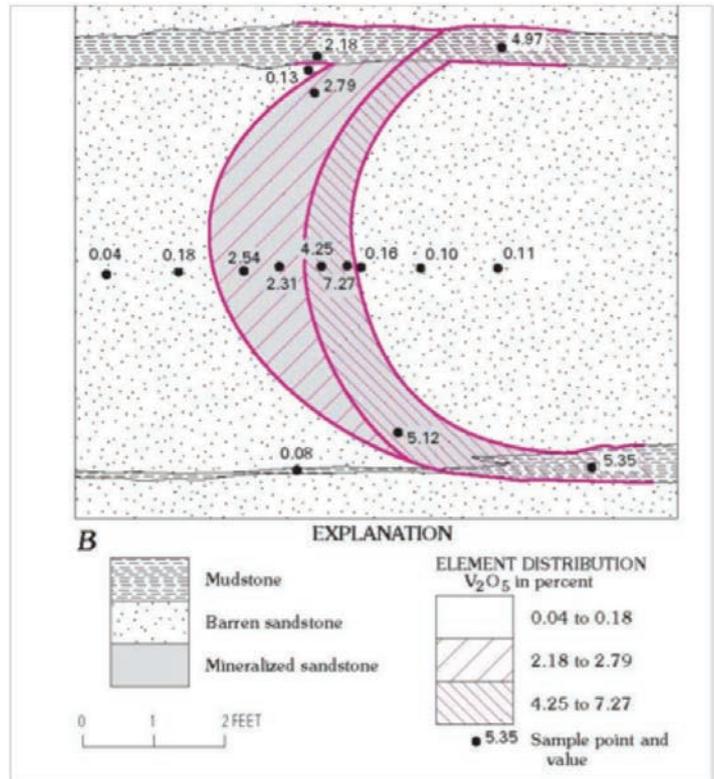
History. The Uravan Mineral Belt has been explored since the late 1880s, when early prospectors discovered radium, vanadium and uranium in the carnotite ores of the Paradox Valley. Since then, these three elements have alternated as the predominant economic resource based upon the market conditions.

Prior to 1930, most of the vanadium produced in the United States came from the roscoelite deposits near Rifle and Placerville in Colorado. The rising demand for vanadium as a steel alloy renewed interest in the vanadium deposits of the Uravan Belt.

In 1943, the Manhattan Project gave new life to the area with the exploration for uranium. The Union Mines Development Corp. was formed, and one of its mandates was to determine the amount of vanadium that was previously mined in the area, with the intention of estimating the recovery of uranium from the vanadium tailings.

A rise in the price of uranium in the late 1970s resulted in a surge of uranium production in the area. However, the drop of uranium prices in 1983 put an end to the uranium and vanadium mining in the area. Since then, the Uravan Mineral Belt has been in a state of inactivity, only to experience a brief period of revival between 2006 and 2008, spurred by a national effort to increase the use of nuclear power for the generation of electricity.

Geology. The uranium-vanadium deposits of the Uravan Belt are emplaced in the Salt Wash member of the Morrison Formation. The Salt Wash member consists of interbedded fluvial sandstone and floodplain-type mudstone units. The uppermost sandstones contain the majority of the ore deposits. A few deposits occur in coarse conglomeratic sandstones in the lower part of the



overlying Brushy Basin member. Records of the Grand Junction office of the U.S. Department of Energy show that production has been derived from nearly 1,200 individual properties within the area.

Individual deposits are localized within permeable, carbonaceous Salt Wash sandstones, some of which are several hundred meters wide and up to a few kilometers long. The tabular orebodies typically are elongated parallel to the sedimentary trends and are concordant with the bedding. The ore averages about 1.2 m (3.9 ft) thick, but, in places, ore thickness approaching 9 m (29.5 ft) has been mined. Individual orebodies may be connected by weakly mineralized rock, but, generally, the boundary of ore and barren rock is abrupt.

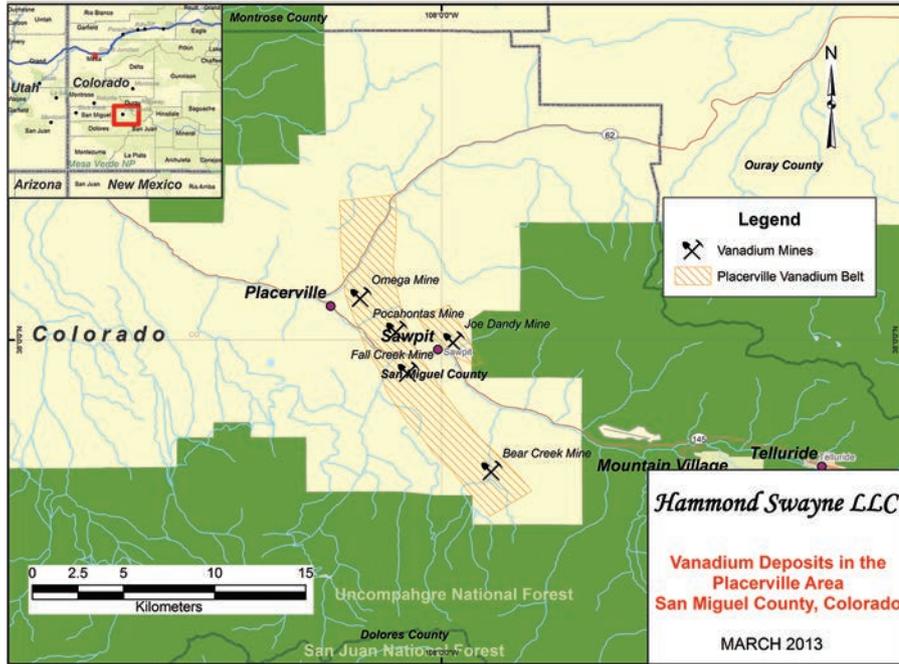
Orebodies ranging from a few tons to large masses containing more than a million tons of ore tend to be clustered within elongated favorable areas. Although most of the mineralized zones in the Salt Wash are tabular and concordant with bedding, the ore in some deposits abruptly crosses bedding in smooth curves called "rolls" by the miners. The rolls in plan are generally narrow, sinuous and decidedly elongated parallel to local sedimentary structures or axes of greatest permeability (Fig. 3).

Some small, high-grade orebodies consist of fossilized log accumulations of carbonaceous material replaced with uranium and vanadium



Figure 4

Vanadium deposits in the Placerville area of San Miguel County.



minerals. The shape and distribution of the deposits are strongly controlled by the transition into shale horizons or other sedimentary features that produce changes in permeability. In general, the highest grade ore occurs next to the oxidation-reduction boundary. Where narrow, gray unoxidized zones extend into red oxidized

sequences, the grade and continuity of the ore improve dramatically.

Mineralogy. Within an orebody, the uranium and vanadium minerals coat sand grains, fill interstices and replace organic material, calcite and quartz. The main minerals are montroseite in the unoxidized areas and corvusite in the partly oxidized deposits. Generally, the amount of vanadium exceeds the uranium in ratios ranging from 3:1 to 10:1, averaging 5:1 in the mined areas. Within the Uravan mineral belt, the vanadium/uranium ratio increases southward from Gateway (3:1) to Slick Rock (8:1). These ratios are based on uranium production since 1947 and include oxidized and unoxidized ores.

Production and potential for future exploration. The largest vanadium deposits in the Uravan Mineral Belt came from the Club Group of mines located 2 km (1.2 miles) southwest of the town of Uravan. The Deremo Mine, located in the Silt Rock area, was the largest mine operation. Others of importance were the Cougar Mine, the Ike and Burro No. 7.

The ore extracted from the mines was tracked to the nearby mills from widely scattered operations. At the mill, the ore was crushed, mixed with common salt and roasted to convert the vanadium minerals into a soluble vanadate, which was then leached with water. Acid was added to the solution, precipitating the sodium vanadate. The precipitate was sacked and shipped in this form, but at most mills it was fused before shipment.

The production at the Uravan Mineral Belt has been recorded in two phases, pre-1946 and from 1946 onward, to reflect the inventory conducted by the Union Mines Development Corp. (Table 1).

During the period from 1947 to 1979, vanadium was recovered from 14.6 kt (16,100 st) with an average grade of 1.24 percent V_2O_5 and containing 187.44 kt (187,443 st) V_2O_5 . This represents 80 percent of the total domestic production of vanadium from sandstone uranium ores.

The areas for potential high-grade vanadium reside in the concave surfaces of the rolls identified previously in this article and in Figure 3. The orientation of the roll surface should be of particular interest to the prospector. The orebodies as a

Table 1

Pre-1946 vanadium production at Uravan Mineral Belt (after Chenoweth, 1981).

Area	Tons	Grade (%)	Kilograms (V_2O_5)
Colorado			
Uravan	424,127	1.78	7,554,988
Slick Rock	89,541	2.38	2,133,734
Gateway	26,236	1.93	505,746
Gypsum Valley	18,779	1.90	356,802
Bull Canyon	16,928	2.18	369,212
Carpenter Ridge	2,722	1.90	51,710
Utah			
La Sal Creek	11,440	1.93	220,788
Moab	9,979	1.80	179,626
Thompson	9,616	2.79	268,295
Polar Mesa	9,172	3.24	297,057
Totals	636,406	1.93	12,328,145
Estimated U_3O_8 : 1,784,235			

Figure 5
Vanadium deposits in the Placerville area of San Miguel County.

whole are aligned in a northeasterly direction, and this alignment seems to be parallel to the elongation of the roll surfaces.

Placerville vanadium deposits, San Miguel County

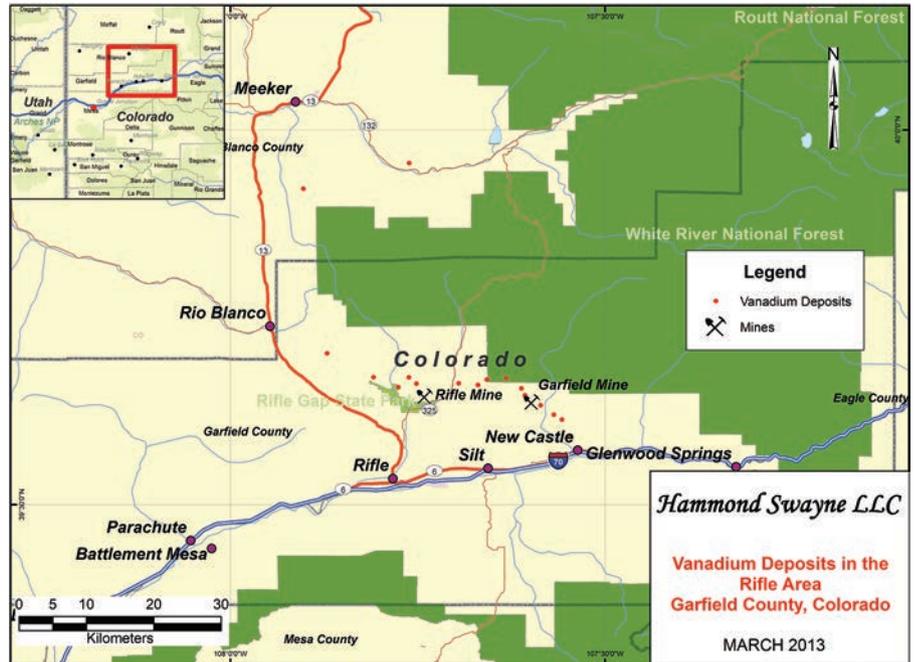
History. The vanadium deposits in the Placerville area were discovered in 1910. Most of the ore was mined between 1910 and 1920, but some production took place during World War II and since the war. Most of the ore contains, in addition to vanadium, minor quantities of U_3O_8 , which was recovered as a byproduct since 1950. The amount of uranium in the Placerville deposits is much less than the ones seen in the Uravan Mineral Belt.

Geology. The vanadium deposits occur in the upper 3-5 m (10-16 ft) of the Entrada Sandstone Formation of late Jurassic age. The Entrada Sandstone Formation is comprised of light-colored sandstone, which is predominantly fine-grained. The Entrada lies on top of the Dolores Formation and underlies the Wanakah Formation. The Morrison Formation lies conformable with the Wanakah. Several igneous dykes are conspicuous along the San Miguel River near Placerville and are probably related to the intrusives in the San Juan Mountains.

The vanadium deposits consist of sandstone impregnated with vanadium minerals. Roscoelite, the vanadium mica, is the principal ore mineral. It occurs as minute flakes coating the sand grains and partly or completely filling the pore spaces between grains. Minor amounts of montroseite occur in high-grade ore, imparting a distinctive greenish-gray color to the sandstone. There is a direct correlation between the darkness of the color and the content of vanadium.

The vanadium deposits occur as a continuous mineralized layer in two separate belts (Fig. 4). The most important belt is 2.4-km wide x 14.5-km long (1.5 miles x 9 miles), extending from Leopard Creek in the north to Big Bear Creek in the south. The smaller belt is exposed for 800 m (2,624 ft) near the Sawpit area and its limits are not well established. The vanadium-bearing layer lies conformant to the bedding on the top 8 m (26 ft). In most places, the layer is only 1- to 2-m (3.2- to 6.5-ft) thick but, locally, the layer thickens abruptly to form lenticular or tabular masses that are minable.

The orebodies are roughly circular to elliptical,



with the log axis tending to be perpendicular to the long axis of the principal belt. The orebodies are irregularly scattered and no geologic or structural control has been recognized. A thin and ill-defined layer of light-green sandstone, present in a finely disseminated chromium-bearing mineral, form an outer boundary to the mineralized vanadium orebodies. This layer has no commercial value but it is a useful horizon marker.

Production and potential for future exploration. The vanadium deposits in the Placerville area have a very low content of uranium. This is evident by the lack of fossilized or carbonaceous material. Among the important mines in the area were the Omega, Fall Creek, Bear Creek and Joe Dandy mines. All of these were mined by open stope and room-and-pillar methods.

The recorded production in the Placerville area was notably smaller than the two other vanadium deposits in Colorado, amounting to 217,724 t (239,995 st) at a grade of 2 percent, totaling 4.354 million kg of V_2O_5 .

The potential for exploration resides south of Big Bear Creek and in the smaller belt within the Entrada Sandstone Formation. Stratigraphy could be a useful tool in the delineation of the potential targets.

Rifle Creek vanadium deposits, Garfield County

History. Vanadium ore in the Rifle Creek area in Garfield County was discovered in 1909.



Production took place intermittently between 1925 and 1954. The Rifle mill was built in 1942 to process large production during the World War II years. Only small-scale operations and development took place after 1949 until 1955, when the operations ceased.

Geology. The vanadium deposits are emplaced in the Navajo and Entrada Sandstone Formation of Jurassic age. Smaller deposits occur in the Morrison Formation, which overlies the Entrada, but are poorly developed. The Chinle and Dakota Formations are also present but have not been developed or studied to the extent of the others. In general, the vanadium deposits in the Rifle Creek area resemble more the characteristics of the deposits in the Placerville area than the ones in the Uravan Mineral Belt.

The Rifle Creek deposits have an extension of approximately 3 km (1.8 miles). The primary vanadium minerals consist dominantly of roscoelite, with a small amount of montroseite. They occupy the sandstone pores but also partly replace the sand grains. The grade ranges between 1 to 3 percent V_2O_5 . There is virtually no trace of carbonaceous material, suggesting a low content of uranium.

The ore deposits are tabular but irregular, with an average thickness of 3 m (10 ft). The mined deposits are distributed in three parallel layers, called Veins No. 1, No. 2 and No. 3, in ascending order. These layers are not concordant with the bedding. As in the case of the deposits in the Uravan area, the vanadium tends to accumulate in the roll surfaces mentioned earlier. Vein No. 1 underlies the entire deposit and is mostly in the Navajo Formation. But it has been known to cross-bed into the Chinle, where it was mined at the Garfield Mine. Vein No. 2 forms several separate orebodies. One in the Navajo and joins the No. 1 Vein in the east end of Rifle Mine. The No. 3 Vein is encapsulated in the Entrada Formation and was mined in the west end of the Garfield Mine.

Each of the three veins is bordered by a thin layer, generally 0.3 cm thick, containing fine grains of metallic sulfides such as galena, sphalerite, chalcopyrite, marcasite, chromium and selenium-bearing minerals. These are known to be good indicators of vanadium mineralization. As in the case of the Uravan deposits, the vanadium-bearing sandstone terminates abruptly on contact with layers of less permeability.

Production and potential for future exploration. The vanadium production in the Rifle Creek area between 1925 and 1954 was

estimated to be 680 kt (750,000 st) at a grade ranging between 1 to 3 percent V_2O_5 , representing approximately 11.3 million kg of V_2O_5 . Most of the ore was processed at the Rifle mill.

The potential for further exploration resides in the lesser developed deposits in the Morrison Formation, which have not been studied in detail. However, the steeply dipping strata along the Grand Hogback may have buried the ore-bearing strata 1.6 or 3.2 km (1 or 2 miles) south of the outcrop of the Navajo and the Entrada Formations.

Another area of interest for prospecting lies to the east in the altered layers at the top of the Chinle Formation.

Conclusions

The development of the vanadium redox battery and the vanadium-lithium phosphate battery offer a compelling story for the storage of mass energy coming from renewable energy sources. Currently, the vanadium market is in a state of balance. However, if this new technology materializes, the world production of vanadium will be insufficient to meet the demand from an industrial-scale application of the vanadium-based batteries.

Currently, there are no primary vanadium mines in the United States. The small production reported in 2011 came as a byproduct in one uranium mine in Utah. The U.S. government does not have stockpiles of vanadium in any of its chemical derivations.

If the utilization of renewable energy sources is to grow to the levels mandated by U.S. energy policy, clearly, new sources of vanadium must be found. This demand is compounded by the increase in the demand of vanadium for metallurgical purposes from China and other emerging countries, as they adopt more rigorous codes for the manufacturing of rebar in the construction industry and steel for the automobile industry. China has passed from being an exporter of vanadium to a net importer of the metal.

The vanadium deposits in the Colorado Plateau have been, historically, the largest producers of vanadium in the United States. All of the vanadium production in the region terminated in the early 1980s when the demand for vanadium subsided along with a drastic drop in the price of uranium. The vanadium deposits in the Colorado Plateau could see a renewed interest in exploration in the coming years and become an important source of this strategic metal for years to come. (References available from the author.) ■