Mineral Commodity Profiles

Rubidium

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U.S. Geological Survey

Open-File Report 03-045

Online Only

Version 1.0

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OVERVIEW

Rubidium is a soft, ductile, silvery-white metal that melts at 39.3 °C. One of the alkali metals, it is positioned in group 1 (or IA) of the periodic table between potassium and cesium. Naturally occurring rubidium is slightly radioactive.

Rubidium is an extremely reactive metal—it ignites spontaneously in the presence of air and decomposes water explosively, igniting the liberated hydrogen. Because of its reactivity, the metal and several of its compounds are hazardous materials, and must be stored and transported in isolation from possible reactants. Although rubidium is more abundant in the earth's crust than copper, lead, or zinc, it forms no minerals of its own, and is, or has been, produced in small quantities as a byproduct of the processing of cesium and lithium ores taken from a few small deposits in Canada, Namibia, and Zambia. In the United States, the metal and its compounds are produced from imported raw materials by at least one company, the Cabot Corporation (Cabot, 2003). Rubidium is used interchangeably or together with cesium in many uses. Its principal application is in specialty glasses used in fiber optic telecommunication systems. Rubidium's photoemissive properties have led to its use in night-vision devices, photoelectric cells, and photomultiplier tubes. It has several uses in medical science, such as in positron emission tomographic (PET) imaging, the treatment of epilepsy, and the ultracentrifugal separation of nucleic acids and viruses. A dozen or more other uses are known, which include use as a cocatalyst for several organic reactions and in frequency reference oscillators for telecommunications network synchronization.

The market for rubidium is extremely small, amounting to 1 to 2 metric tons per year (t/yr) in the United States. World resources are vast compared with demand.

HISTORICAL BACKGROUND

Rubidium, which was discovered by Gustav Kirchhoff and Robert Bunsen in 1861, was the second element, following cesium, to be identified by use of the spectroscope, which they had invented the year before. Rubidium, from the Latin *rubidus*, which means deep red, was named after the red lines in its emission spectrum. Bunsen isolated the carbonate and chloride from the alkaline evaporates of mineral spring water. By reducing rubidium hydrogen tartrate with carbon, he also extracted rubidium metal. Although it does not form any ore minerals of its own, rubidium is a common, if minor, constituent of cesium and lithium ore minerals. Such ores have been located in the United States and several other countries.

Rubidium had no industrial applications until the 1920s when small amounts began to be used in photoelectric cells. Much of the rubidium consumed since then has been used in research of various kinds. Because its chemical and physical properties are so similar to those of cesium, most rubidium used in research or industrially has been consumed as an ingredient of cesium compounds or, if used separately, in applications in which cesium is the more commonly used of the two metals. The quantities of this high-priced and commercially scarce metal that are consumed annually have seldom exceeded about 1 metric ton (t) in the United States (although currently, at the beginning of the 21st century, it may be as high as 2t), and perhaps twice as much worldwide.

DESCRIPTION

Rubidium is a silvery-white metal, soft, ductile, and, with a melting point of only 39.3 °C, liquid at elevated ambient temperatures. It is one of the alkali metals, atomic number 37, atomic weight 85.47, and electron configuration [Kr]5s¹ and is located in period 5, group 1 (or IA) of the periodic table. In nature, rubidium consists of two isotopes that have atomic weights 85 and 87 and that occur in the proportions of 72.2 percent and 27.8 percent, by weight, respectively. ⁸⁷Rb is radioactive with a half-life of 49 billion years; this makes commercially available rubidium sufficiently radioactive to expose a photographic plate in 1 to 2 months. Twenty-four other isotopes of rubidium, all of which are radioactive, have been prepared artificially.

Metallurgically, rubidium forms alloys with the other alkali metals, the alkaline earth metals, antimony, bismuth, and gold; also, it amalgamates with mercury. Chemically, it is the second most electropositive metal, after cesium, and bonds ionically with a wide variety of anions to form compounds, many of which are hygroscopic. In addition to forming water-soluble compounds with common anions and radicals, such as acetate, carbonate, the halides, oxide, nitrate, and sulfate, it forms water-insoluble double halides with antimony, bismuth, cadmium, copper, iron, lead, and several other metals.

Rubidium is an extremely reactive metal; it ignites spontaneously in the presence of air, and reacts violently with oxidizers, halogens and halogenated hydrocarbons, and water—which it decomposes with the liberation of hydrogen. Because of its reactivity, it is stored and shipped in dry mineral oil, other dry saturated hydrocarbons, or an inert atmosphere or vacuum. In quantities of more than about 100 grams (g), it is packaged in sealed stainless steel containers. Smaller quantities are packaged in sealed borosilicate glass ampoules. When glass ampoules are used, they are shipped wrapped and packed in an inert cushioning material, such as vermiculite, each in a metal can. Shipments of the hydroxide, metal, nitrate, oxide, and perchlorate are all treated as hazardous materials, subject to labeling requirements and quantity restrictions. Most other rubidium compounds can be handled and shipped as nonhazardous materials.

Rubidium metal is marketed either as technical grade metal, minimum 99 percent rubidium, or high-purity grade, minimum 99.8 percent rubidium. Rubidium compounds, which are more important commercially than the metal, are prepared in grades that range from 99- to 99.99-percent pure (Wagner, 1997, p. 592-593).

SOURCES OF RUBIDIUM

Although rubidium is not abundant in the Earth's crust—it is 1 of 56 elements that account collectively for the last 0.05 percent of the weight of crustal elements—it cannot be called rare either. At 78 parts per million (ppm) of the crust by weight, it stands 23d in order of abundance of all elements and 16th in order of the metals (Greenwood and Earnshaw, 1998, p. 1294). It is more abundant than some "common" metals, such as copper, lead, or zinc, all of which are mined in quantities measured in millions of metric tons per year, compared with rubidium's maximum of perhaps 2 to 4 t/yr worldwide. It is 30 times as abundant as cesium and 4 times as abundant as lithium, but is obtained only as a byproduct of the extraction of these two metals. The reasons for these disparities are

that the copper, lead, and zinc and lithium and cesium occur in minerals in which they are a principal component and, further, that these minerals are concentrated in some localities into ore deposits. Rubidium, however, forms no minerals of its own and, hence, no rubidium ore deposits. Rather, because it has nearly the same (10 percent larger) ionic radius as potassium and because the latter is more than 2,000 times more abundant than rubidium, most naturally occurring rubidium substitutes in minute amounts for potassium in the lattices of the numerous potassium-containing minerals. Some representative maximum rubidium contents of potassium minerals are microcline (feldspar), 3 percent; muscovite (mica), 2.1 percent; biotite (mica), 4.1 percent; and carnallite and sylvite (evaporites), 0.2 percent (Norton, 1973). Rubidium occurrences are also known in brines in the Salar de Atacama, Chile and in the Caidam Basin, China (Roskill Information Services, Ltd., 1984). Thus, as an almost ubiquitous presence in potassium minerals, rubidium usually remains with the potassium as an impurity as the latter is processed and compounded.

Although rubidium forms no minerals in which it is the predominant metallic element, it occurs in recoverable quantities in certain zoned pegmatites where it is contained in a few cesium and lithium minerals formed late in the pegmatite crystallization sequence. Lepidolite, which is a potassium lithium mica, may contain up to 3.2 percent rubidium, and pollucite, which is a cesium silicate, may contain up to 1.4 percent rubidium (Wagner, 1997, p. 593). Most rubidium has been extracted from lepidolite, but substantial quantities have also been obtained from pollucite; although uncommon in pegmatites, both minerals, when present, are often found together (Norton, 1973: Houston Lake Mining, 2003).

From 1958 until about 1975, rubidium for the U.S. market was supplied largely from a stock of dry mixed alkali carbonates (trade-named Alkarb) that had accumulated at a plant in Texas as a byproduct of the extraction of lithium from imported lepidolite. It contained 20 to 25 percent rubidium carbonate.

Meaningful estimates of world rubidium resources have not been made, but the North American deposits could meet world demand for rubidium for many hundreds of years at present rates of production. For example, an order-of-magnitude estimate that dates from 1985 was made by using estimates of lepidolite and pollucite reserves at the Bernic Lake deposit in Canada (Roskill Information Services Ltd., 1984; Cabot Specialty Fluids, 2003) and the amounts of rubidium that they typically contain; North American (mainly Canadian) rubidium reserves were estimated to amount to about 2,000 t (Carrico and Hedrick, 1985). However, the Pakeagama Lake pegmatite, Ontario has rubidium values that range from 0.97 to 1.2 percent in potassium feldspars that are used for ceramic applications (Houston Lake Mining, 2003). The very small amount of rubidium produced since then would not have diminished that figure appreciably, and further exploration of the ore body could have increased it. Lesser quantities of recoverable rubidium are known to exist in Africa in Namibia and Zambia, and elsewhere in the world. (See Appendix for definitions of resources, reserves, and reserve base.)

PRODUCTION TECHNOLOGIES

Rubidium is obtained as a minor byproduct of the processing of lepidolite and pollucite. These ores are found, often together, in just a few zoned pegmatites around the world and are mined on a small scale by selective methods. The deposits are sought and mined primarily for their lithium content.

Because rubidium is so similar in chemistry to its neighboring alkali metals, it can only be extracted from its ores—lepidolite $[(K, Rb)Li_2AlSi_4O_{10}F_{2}]$, and pollucite $(Cs_2Al_2Si_4O_{12})$ —and separated from potassium and cesium by a lengthy sequence of chemical treatments. The most common process starts with the formation of a solution of mixed alkali alums from the ore minerals either by prolonged leaching with sulfuric acid or by fusion of the ore with gypsum followed by leaching with hot water. The alums are separated from one another and purified by repeated fractional recrystallization. As many as 30 recrystallizations are required to obtain pure rubidium alum $[Rb_2SO_4:Ab_2(SO_4)_3\cdot 24H_2O]$. The purified alum is further treated to yield the hydroxide (RbOH) (Perel'man, 1965, p.101-103; Wagner, 1997, p. 593).

Two other processes have been used to extract rubidium from the mixed alkali carbonate residue generated during the processing of lepidolite and pollucite to extract lithium; this residue was an important feed material in the United States in the 1960s and 1970s. The chlorostannate process yields commercially pure rubidium chloride; the ferrocyanide process yields commercially pure rubidium carbonate (Carrico and Hedrick, 1985).

USES

The chemical and physical properties of rubidium are so similar to those of cesium that the two elements are often used together or interchangeably in many uses. In most such uses, cesium, which is more readily available and at times somewhat cheaper, is used in preference to rubidium. Rubidium has certain uses for which it is either uniquely qualified or is the better suited of the two metals; these are described below (Wagner, 1997; Carrico and Hedrick, 1985; Roskill Information Services Ltd., 1984, p. 23-39).

Specialty glasses, which constitute the leading market for rubidium, are used in fiber optics telecommunications systems and in night-vision devices. The carbonate (Rb₂CO₃) is used as an additive to these types of glass, where it reduces electrical conductivity and improves stability and durability.

The photoemissive property of rubidium, which is that of a surface emitting free electrons when impinged upon by electromagnetic radiation, makes possible the following applications:

- A rubidium-tellurium photoemissive surface is used in photoelectric cells, which are incorporated in a variety of electronic detection and activation devices. It is sensitive to a wide spectrum of radiation from the mid-ultraviolet through the visible into the near-infrared.
- A rubidium-cesium-antimony coating is commonly applied to the photocathodes of photomultiplier tubes, which are used in radiation detection devices, medical imaging equipment, and night-vision devices.

• Rubidium is used as a coating on the electrodes of thermionic converters, which convert heat energy to electrical energy. The ionized rubidium neutralizes the space charge between electrodes, thus enhancing the flow of electrons through the converter; in effect, it increases the power output of the converter.

Rubidium has several applications to the field of medicine, as follows:

- The chloride (RbCl) and several other rubidium salts are used as density-gradient media in the ultracentrifugal separation of viruses and the nucleic acids DNA and RNA.
- Radioactive rubidium is used as a tracer of blood flow.
- Rubidium salts have been used as soporifics and sedatives and for the treatment of epilepsy.
- Rubidium iodide (RbI) has sometimes been substituted for potassium iodide (KI) in treating enlargement of the thyroid gland (goiter).
- Rubidium salts have been used as antishock agents following the administration of arsenical drugs.
- Radiation from ⁸²Rb, which is a decay product of ⁸²Sr, is used in positron emission tomographic (PET) imaging. The rubidium isotope is one of several used in PET, but it is especially well suited for assessing regional blood flow in the heart (myocardial perfusion) and detecting coronary artery disease.

Many of the other uses of rubidium, which are listed below, have been characterized in the trade literature as research uses; perhaps low-volume uses would be a more appropriate term for some of them. Rubidium has, at one time or another, found the following applications:

- Rb has been used as a scavenger of residual oxygen in vacuum electron tubes.
- Early in the development of magnetohydrodynamic power generation, rubidium was considered for use as a seed metal whose function it was to promote ionization of the hot gases that flowed from the combustor section of the generator.
- Traces of rubidium have been used as chemical tags for identification and tracing of manufactured goods of various kinds.
- Rb₂CO₃ has been used in the production of certain synthetic fibers.
- Rubidium has been used as a cocatalyst for some organic reactions.
- The decay of radioactive ⁸⁷Rb to ⁸⁶Sr has been used extensively to determine the age of rocks and minerals.
- Rubidium, which is sometimes used interchangeably with cesium, has been used to make a new kind of atomic clock, the so-called fountain clock, which, with further development, is expected to achieve an accuracy of 1 part in 10¹⁶, which is better than the best timekeeping yet attained (American Institute of Physics, 2000: Reel, 2003).
- The resonant frequency of the ⁸⁷Rb atom is used as the reference frequency in frequency standards and oscillators used in radio and television transmitters, for telecommunications network synchronization, and for satellite navigation and communication.

Cesium and potassium substitute freely for rubidium; sodium, less so. Cesium, germanium, selenium, silicon, tellurium, and several other elements and compounds can

substitute for rubidium as photosensitive materials. Certain materials or processes can substitute for rubidium in several other of its uses, but usually at a cost in efficiency.

INDUSTRY AND MARKET

Although rubidium is not mined in the United States, the metal and its principal compounds are produced by at least one domestic company, Cabot Corporation, from ores mined at its Bernic Lake deposit in Manitoba, Canada. In general, rubidium is extracted from its ores by the same companies that produce cesium, the demand for which is much larger (Cabot Specialty Fluids, 2003). A small number of such companies in Denmark, Germany, Japan, Russia, and the United Kingdom are thought to process rubidium-bearing ores and to produce metal and/or compounds. In addition, a larger number of specialty chemical companies produce various grades of derivative rubidium compounds. Overall, however, the total industry and the market are extremely small compared with those for most metals.

SUPPLY, DEMAND, AND SUSTAINABILITY

All ore required to meet U.S. rubidium demand is imported, probably all from Canada. Some of the required metal and compounds may also be imported from processors in Europe and Asia. No published data on domestic production, imports and exports, or consumption are available.

The supply of lepidolite ore from Canada appears to be stable. Estimates of domestic rubidium consumption from 1965 through 1980 made by the U.S. Bureau of Mines showed a range from 186 kilograms (kg) in 1965 to 816 kg in 1980. An industry source estimates current (2002) domestic consumption to be less than 8,000 pounds of rubidium compounds (Will Pratt, GEO Chemicals Co., oral commun., August 2000). If the carbonate is considered as a proxy for all rubidium compounds, then this quantity would correspond to roughly 2 t (2,000 kg) of contained rubidium. If that figure is valid, then the available North American reserves of rubidium are vast compared with U.S. and world demand.

The mining and processing of rubidium minerals is on such a small scale that environmental hazards or damage are minimal and are not likely to inhibit production. Except for the metal, hydroxide, nitrate, oxide, and perchlorate, which are considered to be hazardous materials, rubidium compounds are innocuous. In any case, the transportation and use of rubidium is on such a small scale that environmental impediments to the use of rubidium also are minimal.

ECONOMIC FACTORS

Because the market is extremely small and the number of producers also small, public trading of rubidium metal or its compounds is not active, and, therefore, quoted prices are nonexistent. The metal is sold by the gram, and the unit price varies greatly with the

amount and purity of the metal purchased. In 2001, for example, one domestic company offered 1-g ampoules of 99.98-percent pure metal for \$52.00. The same metal in 100-g lots was offered at \$9.98 per gram. The producer price typically remains stable for several years. From 1980 through 1991, for example, a representative annual price from one producer (averaged over all lot sizes of up to 50 pounds and over a mix of technical-grade and high-purity grade sales) remained unchanged at \$0.74 per gram. Since then, producer quotes for bulk quantities have not been readily available (Reese, 1999, 2001).

U.S. mine producers are granted a 14-percent depletion allowance on their domestic and foreign production of rubidium. This is a percentage of the income from mine production considered to be a return of capital and, thus, not subject to income tax, a recognition that ore deposits are depletable assets.

Imports of processed rubidium metal are included in the basket category "Alkali metals, other," and subject to a 5.5-percent ad valorem duty. Imports of rubidium compounds are duty free.

OUTLOOK

Rubidium fills niche uses in a very small market. Its rate of consumption appears unlikely to change significantly in the United States or elsewhere. Because the potential supply is vast as compared to foreseen demand and most of it is located in a politically stable environment, no supply disruptions seem likely. Neither the production nor the use of rubidium products appears to be associated with any environmental issues.

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Suggested sources of information on rubidium as a commodity:

U.S. Geological Survey publications Lithium, cesium, and rubidium, in United States Mineral Resources, Professional Paper 820, 1973 Mineral Commodity Summaries, annual Rubidium Worksheet USGS Open File, will call Grecia Matos about this one Other publications American Metal Market, daily Engineering and Mining Journal, monthly Metal Bulletin Monthly Metal Bulletin, weekly Mining Engineering, monthly Mining Journal, weekly Mining Record, weekly Platt's Metals Week, weekly Rubidium, in U.S. Bureau of Mines Mineral Facts and Problems, 1985 Ryan's Notes, weekly

APPENDIX

Definitions of Reserves, Reserve Base, and Resources

The term "resources," as applied to metals, refers to those concentrations of metalbearing minerals in the Earth's crust that are currently or potentially amenable to the economic extraction of one or more metals from them. "Reserves" and "reserve base" are subcategories of resources. "Reserves" refers to the in-place metal content of ores that can be mined and processed at a profit given the metal prices, available technology, and economic conditions that prevail at the time the reserves estimate is made. "Reserve base" is a more-inclusive term that encompasses not only reserves proper, but marginally economic reserves and a discretionary part of subeconomic resources—"those parts of the resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics" (U.S. Bureau of Mines and U.S. Geological Survey, 1980).