THORIUM

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Thorium is a soft, very ductile, silver-gray, heavy, metallic element of the actinide series of elements. It is represented by the chemical symbol Th or the isotopic symbol Th²³². Thorium metal has a very high melting point, 1,750° C. The oxide, which is also called thoria, has the highest melting point of all the binary oxides at about 3,300° C. Th²³² is the most abundant of the four naturally occurring isotopes of thorium. Th²³² emits radioactive alpha particles and has a very long half-life of 1.405 \times 10¹⁰ years. Daughter products of the Th²³² disintegration series produce alpha, beta, and gamma emissions. Most products of the disintegration series have short half-lifes, ranging from 5.75 years to 0.145 second. The final decay product of the Th²³² series is the stable isotope Pb²⁰⁸. Thorium's other naturally occurring isotopes, Th²²⁸, Th²³⁰, and Th²³⁴, have half-lifes of 1.9116 years, 75,380 years, and 24.1 days, respectively.

Thorium was discovered in 1828 by Swedish chemist and mineralogist Jöns Jakob Berzelius (Söderbaum, 1929-31). He named it "thoria", after Thor, the ancient Norse god of thunder. Berzelius isolated the element from a black silicate mineral from the island of Lövö near Brevig, Norway (Weeks and Leicester, 1968, p. 532). Subsequently, the black mineral from which thoria was derived was named thorite. In 1898, thorium's radioactivity was discovered independently by Marie Curie (Curie, 1928) and Gerhard.C. Schmidt (Badash, 1966).

At 7.2 parts per million, thorium is the 39th most abundant of the 78 common elements in the Earth's crust. It is about three times more abundant than uranium and is associated with uranium in igneous rock. Because the primary thorium minerals are more resistant to geochemical and physical weathering, the thorium-to-uranium ratio in sedimentary rock is typically higher than its ratio in igneous source rock. Thorium occurs in several minerals, the most common being the rare earth-thorium-phosphate mineral, monazite, the thorium silicate minerals, thorite (Berzelius, 1829) and huttonite (Pabst, 1951), and the hydrated thorium silicate mineral, thorogummite (Hidden and Mackintosh, 1889).

Domestic consumption of refined thorium products decreased in 1998, according to the U.S. Geological Survey (USGS). The value of thorium metal and compounds used by the domestic industry was estimated to be about \$200,000. Thorium and its compounds were produced primarily from monazite, recovered as a byproduct of processing heavy-mineral sands for titanium and zirconium minerals or tin minerals. Monazite was produced only for its rare-earth content. Only a small portion of the thorium produced was consumed; the rest was discarded as waste. The major monazite-producing countries were Brazil, China, India, Malaysia, and Sri Lanka. Essentially all

thorium compounds, metal, and alloys used by the domestic industry were derived from imports, company stocks, or material sold from U.S. Government stocks (Hedrick, 1997).

Limited demand for thorium, relative to the rare earths, continued to create a worldwide oversupply of thorium compounds and residues. Most major rare-earth processors have switched feed materials to thorium-free intermediate compounds, such as rare-earth chlorides, nitrates, or hydroxides. Excess thorium not designated for commercial use was either disposed of as a radioactive waste or stored for potential use as a nuclear fuel or other application. Principal nonenergy uses have shifted from refractory applications to welding electrodes and lighting.

Problems associated with thorium's natural radioactivity represented a significant cost to those companies involved in its mining, processing, manufacture, and use. Increased costs to comply with environmental regulations, and potential legal liabilities and costs to purchase storage and waste disposal space were the principal deterrents to its commercial use. Health concerns associated with thorium's natural radioactivity have not been a significant factor in switching to alternative nonradioactive materials.

Legislation and Government Programs

Calendar year 1998 included parts of the U.S. Government fiscal years (October 1- September 30) 1998 and 1999. Public Law 105-85, the National Defense Authorization Act for Fiscal Year 1998, was enacted on November 18, 1997. It did not change the previous authorization for the disposal of all stocks of thorium nitrate in excess of the National Defense Stockpile (NDS) goal of 272,155 kilograms (600,000 pounds). Public Law 105-261, the National Defense Authorization Act for Fiscal Year 1999, also called the "Strategic and Critical Stock Piling Act," was enacted on October 17, 1998. The revised annual material plan did not change the disposal of up to 453,592 kilograms (1,000,000 pounds) of thorium nitrate in Fiscal Year 1999, from that of fiscal year 1998, or previous authorizations for the disposal of 2,944,672 kilograms (6,491,891 pounds) of thorium nitrate classified as excess to goal.

Production

Domestic mine production data for thorium-bearing minerals were developed by the USGS from a voluntary survey of U.S. thorium operations. The one mine to which a survey form was sent responded. Although thorium was not produced in the

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United States in 1998, the mine that had previously produced thorium-bearing monazite continued to operate and maintained capacity on standby. Monazite was last produced in the United States in 1994.

Essentially all thorium alloys and compounds used by the domestic industry were derived from imports, company stocks, or materials sold from the NDS. Domestic companies processed or fabricated various forms of thorium for nonenergy uses, such as ceramics, magnesium-thorium alloys, refractories, and welding electrodes.

Consumption

Statistics on domestic thorium consumption are developed by surveying various processors and manufacturers, evaluating import-export data, and analyzing Government stockpile shipments.

Domestic thorium producers reported consumption of 7.0 metric tons of thorium oxide equivalent in 1998, a decrease from the 13 tons produced in 1997 (table 1). The increase in 1997 was primarily the result of a single purchase of thorium for a catalyst application. Nonenergy uses accounted for essentially all consumption.

Thorium oxide has the highest melting point of all the binary metal oxides at $3,300^{\circ}$ C. This property contributed to its use in several refractory applications. High-temperature uses were in ceramic parts, investment molds, and crucibles.

Thorium nitrate was used in the foreign manufacture of lamp mantles for use in incandescent camping lanterns, natural gas lamps, and oil lamps. Thorium mantles provide an intense white light that can be adjusted towards the yellow region by the addition of a small amount of cerium. Thoriated mantles have not been produced domestically since the development of a suitable thorium-free substitute.

Thorium nitrate also was used to produce thoriated tungsten welding electrodes. These electrodes were used to join stainless steels, nickel alloys, and other alloys requiring a continuous and stable arc to achieve precision welds.

The nitrate form was also used to produce thoriated tungsten elements used in the negative poles (cathodes) of magnetron tubes and traveling wave tubes, also known as TWT's. Thorium was used because of its ability to emit free electrons at ambient temperatures when heated in a vacuum. With an improved work function and lower operating temperature, thoriated-cathodes last longer than nonthoriated filaments. Magnetron tubes were used to emit electrons at microwave frequencies in radar systems for air traffic control, surveillances, weather monitoring, and weapon systems and to heat food in microwave ovens.

Thorium was used in other applications as catalysts, electronemitting tubes, elements in special-use light bulbs, fuel cell elements, high-refractivity glass, photoconductive films, radiation detectors, and target materials for x-ray tubes.

In metallurgical applications, thorium was alloyed primarily with magnesium. Thorium metal has a high melting temperature of 1,750° C and a boiling point of about 4,790° C. Magnesium-thorium alloys used by the aerospace industry are lightweight and have high strength and excellent creep

resistance at elevated temperatures. Thorium-free magnesium alloys with similar properties have been developed and are expected to replace most of the thorium-magnesium alloys. Small quantities of thorium were used in dispersion-hardened alloys for high-strength, high-temperature applications.

Thorium was used as a nuclear fuel in the Th²³²/U²³³ fuel cycle. No foreign or domestic commercial reactors are operating with this fuel cycle.

Stocks

Government stocks of thorium nitrate in the NDS were 3,216,828 kilograms (7,091,891 pounds) on December 31, 1998. The NDS inventory included 273,181 kilograms (602,262 pounds) of thorium nitrate allocated to meet the NDS goal requirements and 2,943,646 kilograms (6,489,629 pounds) classified as excess to the goal. No stocks of thorium nitrate were sold or shipped during the year.

The U.S. Department of Energy's (DOE) inventory at yearend was 535,000 kilograms of thorium oxide equivalent contained in metal and various compounds. The DOE contractor, Fernald Environmental Restoration Management Company a subsidiary of Fluor Daniel Fernald, did not ship any stocks during 1998.

Prices

The price of monazite concentrate, typically sold with a minimum 55% rare-earth oxide, including thorium oxide content, free-on-board (f.o.b.) as quoted in U.S. dollars and based on the previous year's U.S. import data, was unchanged at \$400.00 per metric ton. In 1998, no monazite was imported into the United States.

Thorium oxide prices quoted by Rhodia, Inc. (previously Rhône-Poulenc Basic Chemicals Co.) decreased slightly or were unchanged in 1997. At yearend, thorium oxide prices per kilogram f.o.b. Shelton, CT, were unchanged from 1997 at \$82.50 for 99.9% purity and \$107.25 per kilogram for 99.99% purity (Hedrick, 1999).

World Review

Thorium demand continued to remain depressed as industrial consumers expressed concerns with the potential liabilities, cost of complying with environmental monitoring and regulations, and cost increases at approved waste disposal sites.

Current Research and Technology

A researcher at Woods Hole Oceanographic Institute used an isotope of thorium to trace upper ocean processes. In an effort to separate the processes of primary production of particulate organic carbon (POC) and particulate export (as it sinks in the oceanic column) in the surface ocean, Th²³⁴ was used as a tracer. The study concluded that the efficiency of the ocean's biological pump is generally low, with the thorium isotope export level being less than 5% to 10% and that further research is needed to improve global biogeochemical models.

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Exceptions to the general pattern are caused by periodic phytoplankton blooms at certain latitudes that increase POC export rates (Buesseler, 1998).

A U.S. patent was granted to a Tel Aviv University scientist for a light-water thorium reactor. Known as the Radkowsky Thorium Reactor (RTR), the reactor design has the advantage of producing very little radioactive byproducts (i.e., plutonium) that could be used in making nuclear weapons. Funded in part by the U.S. company, Raytheon Corporation, the RTR core can reportedly be retrofitted into existing standard uranium cores in light-water reactors (Siegel, 1997; Wald, 1998). In associated research, the United States and Israel have developed a process to use thorium as a nuclear fuel by using a heterogeneous seed/blanket assembly. The new process, which uses the Th²³²/U²³³ fuel cycle, differs from earlier designs in that the reactor is controlled by using separate fuel management systems instead of mixed fuel components. Thorium is contained in the subcritical blanket to provide an efficient generation area of in-situ fissioning while the supercritical uranium seed supplies the required neutrons to keep the reactor generating. Advantages of the RTR are reductions in the creation of nuclear weapons material, spent fuel and the resulting disposal requirements, and cost because Th²³² is readily available as a byproduct of processing rare-earth elements. Another advantage is that U²³³ is the most fissile of all the nuclide isotopes, producing more neutrons per thermal neutron absorbed (Galperin, Reichert, and Radkowsky, 1997). Implementation of the RTR fuel design was being made on a Russian hexagonal geometry Vodo-Vodyanoy Energetichski Reaktor pressurized-water-reactor (Seth Grae, President, Radkowsky Thorium Power Corporation, oral commun., 1999).

Outlook

Nonenergy uses for thorium in the United States have decreased substantially during the past 8 years. Domestic demand is forecast to remain at 1998 depressed levels unless low-cost technology is developed to dispose of residues. Manufacturers have successfully developed acceptable substitutes for thorium-containing incandescent lamp mantles, paint and coating evaporation materials, magnesium alloys, ceramics, and investment molds. The traditionally small markets for domestic thorium compounds, welding electrodes, and lighting are expected to remain the leading consumers of thorium compounds through the end of the millennium. Thorium's potential for growth in nonenergy applications is limited by its natural radioactivity. Its greatest potential exists in energy applications as a nuclear fuel or subatomic fuel in an industry that accepts radioactivity. The use of thorium as a nuclear fuel may resume in the next decade because of its

ability to generate low quantities of radionuclide byproducts that could be used in weapons. In the long term, high disposal costs, increasingly stringent regulations, and public concerns related to thorium's natural radioactivity are expected to continue to depress its future use in nonenergy applications.

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¹Prior to January 1996, published by the U.S. Bureau of Mines.

TABLE 1 SALIENT U.S. REFINED THORIUM STATISTICS 1/

(Kilograms of thorium dioxide, unless otherwise specified)

| | 1994 | 1995 | 1996 | 1997 | 1998 |
|---|-------------|------------|------------|--------------|------------|
| | 1994 | | | | |
| Exports: Compounds | 7 | 75 | 58 | 241 | 1,130 |
| Imports: | | | | | |
| Thorium ore, including monazite | | 2,800 r/ | 7,070 r/ | 1,400 r/ | |
| Compounds | 3,150 | 20,500 | 26,400 | 13,500 | 7,450 |
| Shipments from Government stockpile excesses | | | | | |
| Consumption, reported nonenergy applications 2/ | 3,590 | 5,390 | 4,920 | 13,000 | 7,000 |
| Prices, yearend, dollars per kilogram: | | | | | |
| Nitrate | \$23.30 3/ | \$23.30 3/ | \$14.32 4/ | \$27.00 4/ | \$23.56 4/ |
| Oxide | \$63.80 3/ | NA | \$64.45 3/ | \$82.50 r/3/ | \$82.50 3/ |
| | | | | | |

r/ Revised. NA Not available.

- 1/ Data are rounded to three significant digits, except prices.
- 2/ All domestically consumed thorium was derived from imported metals, alloys, and compounds.
- 3/ Source: Rhodia, Inc., 99% purity.
- 4/ Source: Bureau of the Census, average import price.

 ${\bf TABLE~2} \\ {\bf U.S.~FOREIGN~TRADE~IN~THORIUM~AND~THORIUM-BEARING~MATERIALS~1/}$

(Kilograms, unless otherwise specified)

| | 1997 | | 199 | 98 | |
|-----------------------------------|----------|-----------|----------|-----------|------------------------------|
| | Quantity | Value | Quantity | Value | Principal destinations, 1998 |
| Exports, compounds | 241 | \$144,000 | 1,130 | \$278,000 | Singapore 543; Japan 334. |
| Imports: | | | | | |
| Thorium ore, monazite concentrate | 1,400 r/ | 8,000 | | | |
| Compounds | 13,500 | 574,000 | 7,450 | 204,000 | France 7,430; India 19. |

r/ Revised.

Source: Bureau of the Census.

 ${\bf TABLE~3} \\ {\bf MONAZITE~CONCENTRATE:~WORLD~PRODUCTION,~BY~COUNTRY~1/~2/} \\$

(Metric tons, gross weight)

| Country 3/ | 1994 | 1995 | 1996 | 1997 | 1998 e/ |
|--------------------|--------|----------|-------|----------|---------|
| Australia e/ | | 200 r/ | | | |
| Brazil e/ | 1,400 | 1,400 | 1,400 | 1,400 | 1,400 |
| China | NA | NA | NA | NA | NA |
| India e/ | 4,600 | 5,000 | 5,000 | 5,000 | 5,000 |
| Malaysia | 426 r/ | 822 r/ | 618 | 688 r/ | 650 |
| South Africa e/ 4/ | 131 | | | | |
| Sri Lanka e/ | 200 | 200 | 200 | 200 | 200 |
| Thailand | 57 | | | 12 r/ | |
| United States | W | | | | 5/ |
| Total | 6,810 | 7,620 r/ | 7,220 | 7,300 r/ | 7,250 |

e/ Estimated. r/ Revised. NA Not available. W Withheld to avoid disclosing company proprietary data; excluded from "Total."

^{1/} Data are rounded to three significant digits.

^{1/}World totals and estimated data are rounded to three significant digits; may not add to totals shown.

^{2/} Table includes data available through May 27, 1999.

^{3/} In addition to the countries listed, Indonesia, North Korea, the Republic of Korea, Nigeria, and the former U.S.S.R. may produce monazite; available general information is inadequate for formulation of reliable estimates of output levels.

^{4/} Monazite occurs in association with titanium sands mining but is not necessarily recovered.

^{5/} Reported figure.