

# **2012 Minerals Yearbook**

# GERMANIUM

## GERMANIUM

## By David E. Guberman

#### The table was prepared by Jesse J. Inestroza, statistical assistant.

In 2012, germanium-bearing concentrates produced at a zinc mine in Alaska owned by Teck Resources Ltd. (Vancouver, British Columbia, Canada) were exported to Teck's facilities in Canada for processing or to processors in Asia and Europe. An intermediate germanium concentrate was produced from zinc concentrates at a mine complex and smelter in Tennessee. Two refineries in New York and Oklahoma produced germanium dioxide, germanium metal, and germanium tetrachloride from manufacturers' scrap, post-consumer scrap, and imported germanium compounds. The U.S. Geological Survey (USGS) estimated that U.S. refinery production of germanium metal from imported primary material and germanium compounds was about 9,300 kilograms (kg) in 2012. The world's total production of germanium in metal and compounds was estimated to be between 100 and 120 metric tons (t), including germanium recovered from zinc concentrates, coal fly ash, and recycled material. Despite an increase in zinc production, the principal source of primary germanium, global germanium metal production estimates remained unchanged from those of 2010 and 2011. The amount of germanium recovered from scrap remained about the same as that in 2011 and accounted for about 30% of the world's total production of germanium.

Germanium is a hard, brittle semimetal that first was used about 60 years ago as a semiconductor material in radar units and as the material for the first transistors. Today, its principal uses include polymerization catalysts for polyethylene terephthalate (PET), a commercially important plastic; a component of glass in telecommunications fiber optic cable; lenses or windows in infrared night-vision devices; and semiconductors and substrates in electronic circuitry and solar cells.

#### **Legislation and Government Programs**

As a strategic and critical material, germanium was added to the National Defense Stockpile (NDS) in 1984. The Defense Logistics Agency (DLA) Strategic Materials reported that no germanium metal was sold in 2012. Germanium was last sold in February 2009 at an average price of \$1,331 per kilogram. As of December 31, 2012, the total inventory of germanium metal held by the DLA was 16,362 kg valued at \$20.7 million. The Annual Materials Plan for fiscal year 2013 (October 1, 2012, through September 30, 2013) did not allocate germanium metal for sale (U.S. Department of Defense, 2013, p. 7).

In 2012, the DLA began moving away from holding a static list of materials and working under the "buy and hold" approach of the past, toward what it characterized as a more flexible and dynamic materials risk management model. The DLA intended to place a greater emphasis on the form in which materials were maintained within the NDS to best meet current and anticipated future applications. To this end, the DLA awarded multiple contracts to upgrade on-hand materials, including a contract to convert 3,000 kg of the germanium ingots to epitaxial wafers for use as substrates required by National Security Space Strategy photovoltaic solar cell applications (U.S. Department of Defense, 2013, p. 2–5).

#### Production

In 2012, germanium intermediates were domestically recovered from zinc concentrates at a smelter in Tennessee. Secondary germanium metal was recovered by secondary processors from end-of-life products, such as decommissioned military vehicles and thermal weapons sights.

The germanium production process yields various germanium compounds and metal for use in specific applications. Germanium is initially recovered from the leaching of zinc residues from zinc refining or coal ash followed by precipitation of a germanium concentrate. All germanium concentrates are purified using similar techniques, regardless of the source of the concentrates. The concentrated germanium is chlorinated and distilled to form the first usable product, germanium tetrachloride, a colorless liquid that is primarily used as a reagent in fiber-optic cable production. Germanium tetrachloride can be hydrolyzed and dried to produce germanium dioxide, another commonly used compound. Germanium dioxide is a white powder and is used to manufacture certain types of optical lenses and as a catalyst in the production of PET resin. Germanium dioxide can be reduced with hydrogen to produce a germanium metal powder, which is subsequently melted and cast into first-reduction bars. The germanium bars are then zone-refined (a refining process that involves melting and cooling germanium bars to isolate and remove impurities and ultimately yield extremely pure germanium) to produce electronic-grade germanium metal. Zone-refined germanium metal can then be grown into crystals and sliced for use as semiconductors or recast into forms suitable for lenses or window blanks in infrared optical devices.

For the first time since 2003, germanium was recovered domestically from zinc concentrates. In the third quarter 2012, Nyrstar NV (Balen, Belgium) began to produce germanium leach, also called residue (an intermediate germanium product), at its Clarksville, TN, zinc smelter. The germanium-bearing zinc concentrates processed at Clarksville were from Nyrstar's Middle Tennessee Zinc mine complex (the Cumberland, Elmwood, and Gordonsville Mines) where mining restarted in 2010 after being idle for about 7 years. The company did not disclose how much germanium leach was produced in 2012 nor its production capacity. Prior to closing in 2003, the Clarksville smelter reportedly had the capacity to produce 20 metric tons per year (t/yr) of germanium-rich residues (Jorgenson, 2004, p. 32.1). The germanium leach produced at Clarksville was most likely exported for further refining. The recovery of germanium at the Clarksville smelter reduced the throughput rate of the roaster, and resulted in lower zinc metal production. In 2012,

Nyrstar worked to improve operating practices at the mines and the smelter so that germanium could be recovered without reducing zinc production at Clarksville. Improvements included regrinding of concentrates from the Gordonsville Mine to increase the throughput rate at the smelter (Nyrstar, NV, 2013, p. 16–17).

Teck Alaska Inc. (a wholly owned subsidiary of Teck Resources) produced germanium-containing zinc concentrates at its Red Dog zinc-lead open pit mine in Alaska. Approximately 30% of the zinc concentrate produced at Red Dog was sent to Teck's metallurgical complex in Trail, British Columbia, Canada. Residues from zinc concentrates were treated in roasters or pressure-leach facilities and purified to produce germanium dioxide, germanium tetrachloride, and other byproduct metals. Teck reported that zinc concentrate production at Red Dog in 2012 was 529,100 t, 8% less than that of 2011 owing to a decrease in mill throughput and ore grades (Teck Resources Ltd., 2013, p. 46).

In 2012, Umicore Optical Materials USA Inc. [a subsidiary of Umicore s.a. (Brussels, Belgium)] continued production of germanium metal and compounds at its plant in Quapaw, OK, and remained the leading domestic producer of germanium and germanium-base materials. Umicore recovered and refined germanium from industry-generated new scrap and from imported germanium compounds. The Quapaw facility refined the material into germanium tetrachloride, germanium metal, and proprietary [chalcogenide glass (GASIR®)] lenses, which were designed for large-scale commercial and military infrared optical systems. In 2011, Umicore began to consolidate all of its germanium-base optics production at its Quapaw facility because it was closer to the main customer base of these products. Umicore anticipated that optics production at its Olen, Belgium, facility would be phased out by yearend 2013. In late 2012, however, Umicore reduced germanium substrate production and the workforce at its Quapaw facility owing to declining market conditions for substrates (Umicore s.a., 2013, p. 49).

Several companies refined or processed imported germanium material. Germanium Corp. of America [a subsidiary of Indium Corp. of America (Clinton, NY)] produced germanium products, including germanium dioxide, germanium metal, and germanium tetrachloride at its facility in Utica, NY. In 2012, Indium Corp. announced plans to open a new minor metals manufacturing plant in Rome, NY. The new plant was to have the capability to produce a range of germanium-base materials (Cammell, 2012).

Sylarus Technologies, LLC (St. George, UT), [a subsidiary of 5N Plus Inc. (Montreal, Quebec, Canada)] produced germanium substrates for optical, semiconductor, and solar applications from germanium dioxide feedstock primarily imported from Canada. In late 2012, Sylarus was awarded a \$1.32 million contract from the DLA to upgrade a portion of the germanium metal held in the NDS to substrates. The DLA intended to have the substrates available for future use in multijunction photovoltaic solar cells for National Security Space Strategy applications (Sylarus Technologies, LLC, 2012).

Voltaix, LLC (Branchburg, NJ) produced germane gas (produced by reducing germanium compounds with hydride reagents and typically used as a doping agent for electronic components) from imported germanium dioxide for use in semiconductors and solar cells. In 2012, Voltaix opened a new germane plant in the Republic of Korea. (More information can be found under the World Review section.) Exotic Electro-Optics, Inc. (Murrieta, CA), E.R. Precision Optical Corp. (Orlando, FL), and Lattice Materials, LLC (Bozeman, MT) produced germanium blanks and lenses for use in infrared optics.

#### Consumption

The USGS estimated that domestic apparent consumption of germanium was about 36,000 kg in 2012, essentially unchanged from that in 2011. Since many of the uses for germanium are in defense-related applications, reductions in Government spending during 2011 and 2012 resulted in reduced germanium consumption. Reports from producers indicated that consumption of germanium blanks for infrared devices and germanium substrates for solar cells declined in 2012 compared with that of 2011. Conversely, germanium substrates consumption for light-emitting diodes (LED) increased during that time period.

Worldwide, the end-use pattern of germanium was estimated to be as follows: infrared optics, 30%; fiber optics, 20%; catalysts for PET, 20%; electronics and solar applications, 15%; and other uses (such as phosphors, metallurgy, and chemotherapy), 15%. The domestic end-use pattern, however, was different, with infrared optics accounting for 50%; fiber optics, 30%; electronics and solar applications, 15%; and other uses, 5%. Germanium was not used in PET catalysts in the United States.

*Infrared Systems.*—Germanium was used in the manufacture of lenses and windows for infrared optical systems owing to its transparency to part of the infrared spectrum and to its high refractive index. (More information can be found in the germanium chapter of the 2011 Minerals Yearbook.) A leading domestic producer of infrared detection and surveillance devices for Government use reported a 13% decline in sales revenue for those products owing to a reduction in procurement activity by governments in the United States and the Middle East in 2012 compared with that in 2011 (FLIR Systems, Inc., 2013a, p. 29; 2013b, p. 7).

As the cost of infrared imaging technology has declined, demand has increased in markets such as airborne law enforcement, automotive night-vision, commercial security, firefighting, and recreational marine applications. FLIR Systems, Inc., a leading domestic thermal imaging device manufacturer, reported that its global revenue from commercial vision systems declined in 2012 compared with 2011 owing to a decline in average unit prices but the volume of units shipped increased. The company reported a 27% compound annual growth rate for global shipments of commercial units from 2007 through 2011 (FLIR Systems, Inc., 2013a, p. 32; 2013b, p. 7, 13).

*Fiber Optics.*—In the fiber-optics sector, germanium tetrachloride is converted to germanium dioxide and used as a dopant (a substance added in small amounts) within the pure silica glass core of optical fibers to increase its refractive index, preventing signal loss while not absorbing light. The Fiber-to-the-Home Council (FTTH) estimated that the number of North American households connected directly into optical fiber networks increased by 13% from March 2011 to March 2012 to about 22.6 million homes. Corning Inc. indicated that global net sales for its telecommunications segment (inclusive of fiber-optic products for fiber-to-the-home and enterprise networking applications) in 2012 were greater than those in 2011 owing to increased consumption of optical fiber and cable in Australia and China. Three Japanese producers, Fujikura Ltd.; Furukawa Electric Co., Ltd.; Sumitomo Electric Industries, Ltd.; and Corning from the United States, accounted for about 90% of global production of germanium-doped silica glass used in optical fiber cable (Fiber-to-the-Home Council, 2012; Roskill's Letter from Japan, 2012; Corning Inc., 2013, p. 25).

Solar Cells.—Germanium-based solar cells were used in space-based applications and terrestrial installations. Demand for satellites increased steadily from 2007 through 2011 owing to demand for commercial, military, and scientific applications. It was estimated that about 400,000 germanium substrates were consumed each year for space-based applications, and the majority of all satellites were powered by germanium-based solar cells. Spectrolab Inc. (a subsidiary of The Boeing Co.) in Sylmar, CA, began adapting space-based solar technology for terrestrial applications in 2001 and has been able to convert concentrated sunlight to electricity at efficiencies as great as 41.6%. Spectrolab manufactured about 7 million terrestrial solar cells in 2011 that contained germanium substrates. In 2012, Spectrolab was nearing completion of an upgrade to its manufacturing facility that was expected to reduce production costs and substantially increase production capacity for terrestrial based solar cells (Boeing Co., The, 2012, p. 11).

*Electronic Components.*—Germanium substrate consumption for production of high-brightness LEDs used in such devices as automobile taillights, cameras, flashlights, mobile telephone display screens, televisions, and traffic signals increased in 2012 compared with that in 2011. Germanium subtrates compare favorably to the leading alternative, gallium arsenide, owing to increased strength, less breakage in production, lower cost, and fewer disposal issues. This continued to be an emerging segment of consumption for germanium substrates. Global sales of high-brightness LEDs were estimated to be about \$15 billion in 2012 compared with \$5 billion in 2009 (Mikolajczak, 2013, p. 19).

*Polymerization Catalysts.*—Estimates indicated that consumption of germanium for PET outside the United States has been declining since 2007, with the exception of an increase in 2011 owing to increased demand for beverage bottles in Japan following the Tohoku earthquake. The decline in consumption for this use continued in 2012. It was estimated that the PET industry consumed about 10,000 kg of germanium dioxide in 2012 compared with nearly 50,000 kg in 2008. Some PET bottle producers were substituting antimony trioxide and titanium-based products for germanium dioxide owing to lower costs (Metal-Pages, 2011; Roskill's Letter from Japan, 2012).

#### Prices

Germanium dioxide prices began the year at about \$1,250 and declined to about \$900 in the late spring, ending the year at \$1,360 per kilogram. Germanium dioxide and metal prices increased sharply during the third quarter, and remained at the higher level during the fourth quarter of 2012. When consumption of germanium appeared to slow early in the year, many producers, particularly in China, reduced production or withheld material from the market, which contributed to higher prices during the fourth quarter of 2012. An announcement that China intended to buy germanium for a national stockpile contributed to price increases, as did curtailed production at three germanium producers in China owing to the Government's environmental policies.

#### **Foreign Trade**

According to the U.S. Census Bureau, imports for consumption of germanium metal (wrought, unwrought, and powder) increased by 33% to 37,500 kg in 2012 from 28,300 kg in 2011. Increased imports from Belgium, Canada, and China outweighed declines from Russia and Taiwan. In 2012, China, Belgium, Russia, and Canada, in descending order of quantity, accounted for 96% of germanium metal imported into the United States (table 1). The estimated germanium content of the germanium dioxide imported in 2012 was about 11,000 kg compared with 10,000 kg in 2011. Canada accounted for about one-half of germanium dioxide imports in 2012.

Domestic exports of germanium metal and articles thereof, including waste and scrap, were estimated to be about 15,300 kg in 2012, based on trade data from the U.S. Census Bureau; adjusted by the USGS to exclude scrap. Belgium, Canada, and Russia accounted for the majority of germanium exported from the United States in 2011. The estimated germanium content of germanium dioxide exported from the United States in 2012 was less than 100 kg.

#### World Review

In 2012, the world's total production of germanium was estimated to be between 100 and 120 t. This comprised germanium recovered from zinc concentrates, coal fly ash, and recycled material. The recycling level remained about the same as that in 2011 and supplied about 30% of the world's total production of germanium. Owing to the value of refined germanium, new scrap generated during the manufacture of fiber-optic cables, infrared optics, and substrates is typically reclaimed and fed back into the production process. Recycling of germanium from used materials, such as fiberoptic window blanks in decommissioned military vehicles or fiber-optic cables, has increased during the past decade. Worldwide, primary germanium was recovered from zinc residues in Belgium and Canada (concentrates shipped from the United States), coal ash and zinc residues in China (multiple sources), zinc residues in Finland [concentrates from Congo (Kinshasa)], and coal ash in Russia. The vast majority of germanium production was concentrated in Canada and China.

As a byproduct metal, the supply of germanium was heavily reliant on zinc production, which increased on a global basis in 2012 primarily owing to increased production in China. While clearly an important factor, an increase in zinc mine production may not be an indicator of a corresponding change in the supply of germanium. It has been estimated that less than 5% of the germanium contained in zinc concentrates reaches refineries that are capable of extracting and producing germanium (Mikolajczak, 2013, p. 9).

**Belgium.**—Umicore produced germanium metal, germanium tetrachloride for fiber optics, germanium substrates, and germanium optical products at its refining and recycling plant in Olen. The company reported that its sales of germanium substrates decreased in 2012 from those of 2011 owing to a decline in consumption for use in solar cells. Sales of substrates used in LEDs increased in 2012 compared with those in 2011. Consumption of germanium blanks for optics applications decreased substantially as a result of a reduction in government-sponsored programs (Umicore s.a., 2013, p. 49).

*Canada.*—The metallurgical complex operated by Teck in Trail consisted of six major metallurgical plants, one fertilizer plant, and two specialty metal plants that produced byproduct metals, including germanium. Historically, Teck has been one of the leading germanium producers in the world. Teck did not disclose germanium production information to the public. The last year for which the company released production data was 2007, when Teck produced about 40,000 kg of germanium dioxide at Trail. Based on trade data published by the Canadian Government, Canada exported about 36,300 kg of germanium contained in germanium dioxide in 2012 compared with about 25,200 kg in 2011. The leading destinations of exported germanium dioxide were Japan, 60%; the Republic of Korea, 14%; the United States, 14%; and Germany, 5% (Statistics Canada, 2013).

*China.*—China continued to be the leading global producer of germanium metal and germanium compounds, producing germanium-bearing coal ash and zinc ore. In 2012, five or six producers accounted for the majority of the estimated 80 to 100 t of germanium metal and germanium compounds produced in China. The Chinese Government attempted to limit exports of raw materials and encourage the export of more processed products, such as germanium ingots and optical lenses, through export tax rebates on those products. In 2011 and 2012, the Government imposed a 5% export tax on germanium dioxide.

In June, Yunnan Germanium Corp., a leading global germanium dioxide producer, and the Hanergy Holding Group, a solar cell producer, agreed to a supply contract. The contract terms called for Yunnan Germanium to supply the Hanergy Group with 375 t of germanium dioxide from July 2012 to yearend 2018 for the production of germane for use in solar cells. The sales quantity was thought to account for the majority of Yunnan Germanium's production, limiting germanium availability for other consumers and possibly contributing to third quarter price increases. By October, however, owing to a downturn in the solar cell market, the terms were renegotiated and called for the Hanergy Group to purchase 20 t of germanium in 2012 and then to buy germanium on-demand during the remaining years of the contract (Metal Bulletin, 2012; Yang, 2012d).

In August, China's State Reserve Bureau (SRB) planned to purchase germanium from domestic producers for the national stockpile. The SRB wanted to acquire 20 t of germanium for the stockpile and four companies were approved to sell material to the SRB. The SRB postponed its stockpile tender owing to a lack of germanium supply from the approved producers. Two of the producers closed temporarily to install environmental protection equipment and another offered to sell germanium at a price that was too high for the SRB (Yang, 2012a, b).

Japan.—Japanese consumption of germanium was met entirely by imports. In 2012, Japan imported 28,500 kg of germanium dioxide, a 14% increase from that in 2011 but substantially less than peak imports of 48,100 kg in 2007. The increase in 2012 was primarily attributed to greater consumption of germanium tetrachloride for use in the production of optical fiber. In 2012, Japanese producers manufactured 45 million kilometers of optical fiber for cable, a 28% increase from that in 2011 (Roskill's Letter from Japan, 2010; 2012; 2013a, b; Yang, 2012c).

*Korea, Republic of.*—In mid-2012, Voltaix announced that it had started germane production at the newly established Voltaix Korea, Ltd. manufacturing site in South Chungcheong Province. The plant was expected to have the capacity to produce 30 t/yr of germane using technology developed at the Voltaix germane operation in Branchburg (Voltaix, LLC, 2012).

*Russia.*—During the past few years, it was thought that germanium production and exports had increased in Russia. Germanium and Applications Ltd. (Moscow) recently began recovering germanium from fly ash from coal mined at the massive Pavlovskoye coal deposit in the Russian Far East. The company reported that coal production from the open pit mine could yield as much as 21 t/yr of germanium, and its facilities in Novomoskovsk and Moscow had the capability to produce germanium oxide and metal, germanium blanks for optical use, and substrates for electronics (Germanium and Applications Ltd., 2013).

#### Outlook

Global germanium consumption is likely to increase, possibly slightly, during the next several years owing to the growth that is expected in the major end-use sectors. Germanium-based optical blanks and windows that are incorporated in infrared devices were expected to continue to be heavily used by military and law enforcement agencies. Increased substitution of specialty glass for pure germanium in infrared applications will continue to be attractive to some consumers owing to the high price of germanium. New applications for these products in commercial and industrial markets were also expected to become more prevalent and represented significant potential consumption growth. In China, germanium producers were expected to continue to expand to downstream products and were expected to manufacture finished infrared products for export.

Global demand for fiber-optic cable, led by the emerging Asian economies and Brazil, was forecast to increase at a compound annual growth rate of 5% to 7% through 2015. Global support for the increased use of solar energy during the next several years is expected to increase demand for germanium substrates that are used to manufacture highefficiency multijunction solar cells. Satellites launched for defense and private industry were expected to continue to fuel consumption of germanium substrates in solar cells. As energy conversion efficiencies continue to improve, terrestrial-based solar cell markets could significantly boost annual germanium substrate consumption. Germanium substrate use in highbrightness LEDs was expected to continue to increase substantially through 2014. As an alternative to gallium arsenide in LEDs, germanium substrates are less expensive, stronger, and do not contain toxic substances (Mikolajczak, 2013).

On the supply side, the Middle Tennessee Zinc mine complex is expected to ramp up production during the next few years. Several germanium recovery projects in China that recently began production or were in late stages of development could bring more germanium to the market if the near-term demand continues to increase. The availability of recycled germanium recovered from end-of-life products, such as fiber optics, military vehicles, and solar cells, was expected to increase during the next two decades as aging products are taken out of service. Overall, the germanium market is expected to remain tight during the next several years owing to expanding demand in emerging uses and to limited sources of additional supply.

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#### TABLE 1

### U.S. IMPORTS FOR CONSUMPTION OF GERMANIUM METAL, BY COUNTRY $^{\rm l,\,2}$

	2011		2012	
	Gross weight		Gross weight	
Country	(kilograms)	Value	(kilograms)	Value
Belgium	5,300	\$7,900,000	6,490	\$9,160,000
Canada	215	235,000	2,360	1,030,000
China	17,400	24,600,000	23,700	30,700,000
Germany	776	1,120,000	530	841,000
Hong Kong			582	596,000
Russia	4,040	5,140,000	3,490	4,220,000
Taiwan	500	301,000		
United Kingdom			331	368,000
Other	83	30,400	4	14,000
Total	28,300	39,400,000	37,500	46,900,000

-- Zero.

<sup>1</sup>Data are rounded to no more than three significant digits; may not add to totals shown. <sup>2</sup>Data include wrought, unwrought, and powder, but exclude germanium dioxide.

Source: U.S. Census Bureau.