

# **2013 Minerals Yearbook**

# **GERMANIUM [ADVANCE RELEASE]**

## GERMANIUM

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In 2013, two domestic zinc operations produced recoverable byproduct germanium. In Alaska, the Red Dog Mine, owned by Teck Alaska Inc., a wholly owned subsidiary of Teck Resources Ltd. (Vancouver, British Columbia, Canada), produced zinc concentrates that were exported to Teck's facilities in Canada for processing or to processors in Asia and Europe. In Tennessee, the Clarksville zinc smelter owned by Nyrstar NV (Balen, Belgium) produced and exported germanium leach concentrates recovered from processing zinc concentrates from its Middle Tennessee mine complex. Two refineries in New York and Oklahoma produced germanium dioxide, germanium metal, and germanium tetrachloride from manufacturers' scrap, postconsumer 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 9,500 kilograms (kg) in 2013. The world's total production of germanium in metal and compounds was estimated to be about 155,000 kg, including germanium recovered from zinc concentrates, coal fly ash, and recycled material. The increase in global production from that in 2012 was due to an increase in production in China. The amount of germanium recovered from scrap remained about the same as that in 2012 and accounted for about 30% of world production of germanium metal.

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. It is commercially available as tetrachloride, high-purity oxide, and forms of metal. Its current principal uses include lenses or windows in infrared night-vision devices; a component of glass in telecommunications fiber-optic cable; polymerization catalysts for polyethylene terephthalate (PET), a commercially important plastic; 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 Strategic Materials (DLA Strategic Materials) reported that no germanium metal was sold in 2013. Germanium was last sold in February 2009 at an average price of \$1,331 per kilogram. As of December 31, 2013, the total inventory of germanium metal held by the DLA Strategic Materials was 16,362 kg valued at \$24.8 million. The Annual Materials Plan for fiscal year 2014 (October 1, 2013, through September 30, 2014) did not allocate germanium metal for sale. In fiscal year 2012, the DLA Strategic Materials awarded two contracts to convert 3,000 kg of the germanium ingots held in the stockpile to epitaxial wafers for use as substrates required by National Security Space Strategy photovoltaic solar cell

#### Production

In 2013, germanium intermediates were domestically recovered from zinc concentrates at a smelter in Tennessee. About 5,000 kg of 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 zincrefining residues or coal fly ash, followed by precipitation of a germanium concentrate. The concentrate, regardless of its source, is chlorinated and distilled to form the first usable product, germanium tetrachloride, a colorless liquid that is primarily used in fiber-optic cable production. Germanium tetrachloride can be hydrolyzed and dried to produce germanium dioxide, a white powder that is used to manufacture certain types of optical lenses and as a catalyst in the production of PET resin. Germanium metal powder is produced through the reduction of germanium dioxide with hydrogen. The powder 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) to produce high-purity electronic-grade germanium metal. Zone-refined germanium metal is then grown into crystals and sliced for use as semiconductors or recast into forms suitable for lenses or window blanks for infrared optical devices.

In the third quarter of 2012, Nyrstar NV began to produce germanium leach, also called residue (an intermediate germanium product), at its Clarksville zinc smelter. The germanium-bearing zinc concentrates processed at Clarksville were from Nyrstar's Middle Tennessee zinc mine complex (the Cumberland Mine. Elmwood Mine, and Gordonsville Mine and mill), where mining restarted in 2009 after being idle for about a year. The company did not disclose how much germanium leach was produced in 2013. The Clarksville smelter reportedly had the capacity to produce 20 metric tons per year (t/yr) of germanium-rich, zinc-refining 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 2013, Nyrstar reported that it had improved processing and recovery of gallium and germanium from the Middle Tennessee mine complex. The Middle Tennessee mine complex commissioned a regrind processing circuit at the mill to deliver more finely ground concentrates to the smelter. As a result, Clarksville was

able to produce an upgraded and more valuable product with higher gallium and germanium content (Nyrstar NV, 2013, p. 16–17; 2014, p. 22).

Teck Alaska 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, for processing. 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 2013 was 551,300 t, 4% more than that of 2012 owing to increased mill throughput and recovery rate (Teck Resources Ltd., 2014, p. 53).

In 2013, Umicore Optical Materials USA Inc. [a subsidiary of Umicore s.a. (Brussels, Belgium)] produced 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 germaniumbase optics production at Quapaw to be 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 early 2013, however, Umicore reduced germanium substrate production and the workforce at Quapaw owing to reduced demand for terrestrial photovoltaics (Joplin Globe, The, 2013; Umicore s.a., 2014, 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.

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 Strategic Materials to upgrade a portion of the germanium metal held in the NDS to substrates. The DLA Strategic Materials intended to have the substrates available for future use in multijunction photovoltaic solar cells for National Security Space Strategy applications. As of yearend 2013, none of the germanium held in the stockpile had been upgraded to substrates (Sylarus Technologies, LLC, 2012).

#### Consumption

The USGS estimated that domestic apparent consumption of germanium metal (including metal content of compounds) was about 38,000 kg in 2013, essentially unchanged from that in 2012. Since many of the uses for germanium are in defenserelated 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 2013 compared with that of 2012. Conversely, consumption of germanium for fiber optics increased during that time period.

The worldwide end-use pattern of germanium was estimated to be fiber optics, 30%; infrared optics, 20%; polymerization catalysts, 20%; electronics and solar applications, 15%; and other uses (such as phosphors, metallurgy, and chemotherapy), 15%. The domestic end-use distribution was different and was estimated to be fiber optics, 40%; infrared optics, 30%; electronics and solar applications, 20%; and other uses, 10%. Germanium was not used in polymerization 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 2012 USGS Minerals Yearbook, volume I, Metals and Minerals. Global demand for germanium used in infrared products reportedly declined in 2013 partially owing to the European debt crisis. A leading domestic producer of infrared surveillance devices reported a 6% decline in sales revenue for those products owing to reduced purchases by the U.S. Government in 2013 compared with those in 2012 (Yi, 2013a; FLIR Systems, Inc., 2014, p. 32–33).

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) in the pure silica glass core of optical fibers to increase refractive index, preventing signal loss while not absorbing light. Global consumption of germanium for use in fiber optics increased in 2013 owing to expansion of telecommunications networks in developing nations. The Fiber-to-the-Home Council (FTTH) estimated that as of May 2013, 22.7 million North Americans were connected directly into optical fiber networks, and about 9.7 million of those households subscribed to the service offered. The organization estimated that about \$18 billion would be invested in expanding the FTTH network infrastructure in North America from 2013 to 2017. Three producers in Japan (Fujikura Ltd.; Furukawa Electric Co., Ltd.; and Sumitomo Electric Industries, Ltd.) and Corning Inc. in the United States accounted for about 90% of global production of germaniumdoped silica glass used in fiber-optic cable (Fiber-to-the-Home Council, 2013; Yi, 2013a; Roskill's Letter from Japan, 2015).

*Solar Cells.*—Germanium-based solar cells were used in space-based applications and terrestrial installations. Demand for satellites increased steadily from 2007 through 2013 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. A leading germanium substrate producer reported that sales of substrates for use in terrestrial photolovtaics declined in 2013 compared to those in 2012. Spectrolab Inc. (a subsidiary of The Boeing Co.) in Sylmar, CA, began adapting space-based solar technology for terrestrial applications in 2001, and in 2013, a Spectrolab

solar cell (using a germanium substrate) set a world efficiency record by converting 37.8% of solar energy. The achievement was verified by the U.S. Department of Energy's National Renewable Energy Laboratory in Golden, CO. The cell converted energy into electricity using a high-efficiency multijunction solar cell, created from two or more materials. The record was set without concentration, the common practice of having lenses or mirrors focus solar rays on the cells (Boeing Co., The, 2013; Umicore s.a., 2014, p. 31).

*Electronic Components.*—According to a leading producer, germanium substrate consumption for production of high-brightness light-emitting diodes used in such devices as automobile taillights, cameras, flashlights, mobile telephone display screens, televisions, and traffic signals, decreased in 2013 compared with that in 2012. Germanium substrates compare favorably to the leading alternative, gallium arsenide, owing to increased strength, less breakage during production, lower cost, and fewer disposal issues (Umicore s.a., 2014, p. 31).

*Polymerization Catalysts.*—Estimates indicated that consumption of germanium for PET outside the United States has been declining since 2012, owing to germanium price increases that led to substitutions. The majority of germanium consumed for PET resin production took place in Japan where producers have substituted lower cost antimony- and titaniumbased products for germanium dioxide catalysts. In 2013, Japan imported 18,700 metric tons (t) of germanium dioxide (gross weight), a 34% decline from that in 2012 (Roskill's Letter from Japan, 2015).

#### Prices

Germanium dioxide prices began the year at about \$1,360 per kilogram and declined to about \$1,300 per kilogram in early February, ending the year at \$1,225 per kilogram. Germanium metal prices began the year at about \$1,640 per kilogram and ended the year at \$1,900 per kilogram. The price increases at yearend were partially driven by stockpiling activities in China. Germanium metal and dioxide prices continued a 5-year upward trend, having increased more than doubled since 2009.

#### **Foreign Trade**

According to the U.S. Census Bureau, imports for consumption of germanium metal (wrought, unwrought, and powder) decreased by 9% to 34,300 kg in 2013 from 37,500 kg in 2012. Decreased imports from Belgium, China, Germany, Hong Kong, Russia, and the United Kingdom more than offset a slight increase from Canada and Japan. In 2013, China, Belgium, Canada, and Russia, in descending order of quantity, accounted for 98% of germanium metal imported into the United States (table 1). The estimated germanium content of the germanium dioxide imported in 2013 was about 11,400 kg compared with 11,000 kg in 2012.

Domestic exports of germanium metal and articles thereof were estimated to be about 12,400 kg in 2013, based on trade data from the U.S. Census Bureau that were adjusted by the USGS to exclude scrap. Belgium, Canada, and Russia accounted for the majority of germanium exported from the United States in 2013. The estimated germanium content of germanium dioxide exported from the United States in 2013 was less than 100 kg.

#### **World Review**

In 2013, the world's total production of germanium was estimated to be about 155,000 kg, which consisted of germanium recovered from zinc concentrates, coal fly ash, and recycled material. The recycling level remained about the same as that in 2012, and scrap was estimated to have 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 was typically reclaimed and fed back into the production process. Recycling of germanium from used materials, such as fiber-optic window blanks from 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 fly ash and zinc residues in China (multiple sources), zinc residues in Finland [concentrates from Congo (Kinshasa)], and coal fly 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 was essentially unchanged in 2013 from that in 2012. Although an important factor, global changes 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 refinery and recycling plant in Olen. The company reported that its sales of germanium substrates decreased in 2013 from those of 2012 owing to a decline in consumption for use in terrestrial-based solar cells, which more than offset an increase in consumption of substrates for space-based applications. Consumption of germanium blanks for optics applications decreased substantially as a result of a reduction in Government-sponsored programs. Sales of germanium tetrachloride for use in fiber optics increased in 2013 from those in 2012 (Umicore s.a., 2014, p. 31–32).

*Canada.*—The metallurgical complex operated by Teck in Trail included two specialty metal plants that produced byproduct metals, including germanium. Historically, Teck has been one of the leading germanium producers in the world. The last year for which the company released production data was 2007, when Teck produced about 40,000 kg of germanium dioxide at Trail (Teck Cominco Ltd., 2008).

*China.*—China continued to be the leading global producer of germanium metal and germanium compounds, which were recovered from germanium-bearing coal fly ash and zinc ore. In 2013, five or six producers accounted for the majority of the estimated 110 t of germanium metal (content) and germanium compounds (content) produced in China. The capacity utilization rate for germanium producers in 2013 was estimated to be about 55% (Yi, 2013b). The Government of China attempted to limit exports of raw materials and to encourage the export of more processed products, such as germanium ingots and optical lenses, through export tax rebates on those products. In 2013, the Government continued to impose a 5% export tax on germanium dioxide that has been charged since 2011.

In 2013, Yunnan Germanium Corp., a leading global germanium metal producer, produced 63 t and sold 78 t of germanium metal, increases of 45% and 95%, respectively, from those in 2012. The company planned to produce 30 t of germanium metal in 2014, about one-half of 2013 production, and sell more value-added products, including infrared lenses and substrates for solar cells. Accordingly, the company announced plans to expand its capacity to produce lenses for infrared optics. This strategy was consistent with many Chinese firms that were trying to sell more downstream products instead of raw materials (Yi, 2014a, b).

In 2013, China's State Reserve Bureau purchased 30 t of germanium for the national stockpile from their domestic producers for about \$2,000 per kilogram, higher than the prevailing market price at the time. All of the material was expected to be delivered during the first quarter of 2014. According to industry sources, the stockpile purchases were intended to "boost market confidence" and encourage producers to increase their prices (Zhao, 2013).

*Russia.*—During the past few years, it was thought that Russian germanium production and exports had increased. 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 Moscow and Novomoskovsk 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 during the next several years in the fiber-optics sector, balanced by limited increases in consumption for other applications. Germanium-based optical blanks and windows that are incorporated in infrared devices are expected to continue to be heavily used by military and law enforcement agencies; however, cuts in Government military spending could limit growth in this area. 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 infrared products that use germanium lenses in commercial and industrial markets are also expected to become more prevalent. In China, germanium producers are expected to continue to expand to downstream products and to manufacture finished infrared products for export.

Global demand for fiber-optic cable, led by the emerging Asian economies and Brazil, is 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 are also expected to continue to fuel consumption of germanium substrates in solar cells. As energy conversion efficiencies continue to improve, terrestrialbased solar cell markets could significantly boost annual germanium substrate consumption (Mikolajczak, 2013).

On the supply side, 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, is 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 limited sources of supply.

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 TABLE 1

 U.S. IMPORTS FOR CONSUMPTION OF GERMANIUM METAL, BY COUNTRY<sup>1, 2</sup>

20	2012		2013	
Gross weight		Gross weight		
(kilograms)	Value	(kilograms)	Value	
6,490	\$9,160,000	5,620	\$6,970,000	
2,360	1,030,000	2,450	1,130,000	
23,700	30,700,000	23,200	36,900,000	
530	841,000	341	836,000	
582	596,000	193	368,000	
		200	354,000	
3,490	4,220,000	2,320	3,080,000	
331	368,000			
4	14,000	11	27,100	
37,500	46,900,000	34,300	49,700,000	
	Gross weight (kilograms)           6,490           2,360           23,700           530           582           3,490           331           4	Gross weight (kilograms)         Value           6,490         \$9,160,000           2,360         1,030,000           23,700         30,700,000           530         841,000           582         596,000           3,490         4,220,000           331         368,000           4         14,000	Gross weight (kilograms)         Value (kilograms)         Gross weight (kilograms)           6,490         \$9,160,000         5,620           2,360         1,030,000         2,450           23,700         30,700,000         23,200           530         841,000         341           582         596,000         193             200           3,490         4,220,000         2,320           331         368,000            4         14,000         11	

-- 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.