

2016 Minerals Yearbook

GERMANIUM [ADVANCE RELEASE]

GERMANIUM

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In 2016, two domestic zinc operations produced recoverable byproduct germanium. In Alaska, the Red Dog Mine, owned by Teck Resources Ltd. (Canada), produced zinc concentrates that were exported to Teck's facilities in Canada for processing and to processors in Asia and Europe. Teck Washington Inc. (a wholly owned subsidiary of Teck Resources) operated the underground Pend Oreille zinc and lead mine in northeast Washington State. All concentrates were shipped to Teck's facilities in Canada for processing. In Tennessee, the Clarksville zinc smelter, owned by Nyrstar NV (Belgium), was thought to have not produced byproduct germanium concentrates because the Middle Tennessee mine complex was put on care-and-maintenance status in December 2015. Operations are not scheduled to resume until 2017 (Nyrstar NV, 2016c). The U.S. Geological Survey (USGS) estimated that in 2016, the combined U.S. refinery production of germanium metal recovered from end-of-life products, such as decommissioned military vehicles and thermal weapons sights, industrygenerated scrap, and imported germanium dioxide, was between 5,000 and 15,000 kilograms (kg). The total world production (excluding the United States) of germanium in metal and compounds, including germanium recovered from zinc concentrates, coal fly ash, and recycled material, was estimated to be about 126,000 kg, 14% less than 2015. The amount of germanium recovered from scrap in 2016 was estimated to be 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 various 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.

The germanium production process yields various germanium compounds and metal for use in specific applications. Germanium is initially recovered through the leaching of zinc-refining residues or coal ash, followed by precipitation of a germanium concentrate from the leachate. The concentrate, regardless of its source, is chlorinated, distilled, and purified 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 in the manufacture of 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, and first-reduction bars are cast from melted powder. The germanium bars are zone-refined (a process that involves

melting and cooling to isolate and remove impurities) to produce high-purity electronic-grade germanium metal. Zonerefined germanium metal is grown into crystals that are sliced for use as semiconductors or recast into forms suitable for lenses or window blanks for infrared optical devices.

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 2016. Germanium was last sold in February 2009 at an average price of \$1,331 per kilogram. As of December 31, 2016, the total inventory of germanium metal held by DLA Strategic Materials was 13,364 kg. The Annual Materials Plan (AMP) for fiscal year 2017 (October 1, 2016, through September 30, 2017) allocated 5,000 kg of germanium metal for potential upgrades or disposals, and DLA Strategic Materials could potentially acquire up to 1,000 kg of germanium metal in fiscal year 2017. In fiscal year 2012, 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 the National Security Space Strategy photovoltaic solar cell applications. As of yearend 2016, 101,939 wafers were held in the stockpile compared with 101,899 held at yearend 2015 (Defense Logistics Agency Strategic Materials, 2016a, b).

In 2015, DLA Strategic Materials entered into a collaborative program with Army Contracting Command–Warren (ACC–Warren) and Anniston Army Depot (ANAD) to recover germanium from excess Army components. Under an ACC–Warren contract, germanium-containing end-of-life components started to be shipped from ANAD to a contractor. The contractor was to demilitarize the components, remove any radioactive coatings from the germanium lenses and windows, and send the germanium scrap to the NDS. In fiscal year 2016, more than 700 kg of clean germanium scrap was shipped to the NDS (U.S. Department of Defense, 2017, p. 6, 8).

Production

Teck Alaska Inc. 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-in-concentrate production at Red Dog increased by 3% to 583,000 metric tons (t) in 2016 from 567,000 t in 2015 owing to increased mill throughput with softer ores processed. Teck

projected that zinc production at Red Dog would decrease in the next few years, ranging from 545,000 to 565,000 t in 2017 and from 500,000 to 525,000 metric tons per year (t/yr) in 2018 through 2020 (Teck Resources Ltd., 2017a, p. 36–38, 45).

In December 2014, Teck restarted the Pend Oreille Mine in Washington State. The mine produced germanium-containing zinc concentrates that were processed at Teck's Trail plant. Zinc-in-concentrate production at Pend Oreille increased to 34,100 t in 2016 from 30,700 t in 2015. Teck projected that zinc production in 2017 would increase further to between 35,000 and 40,000 t, and there was potential to extend the mine life to at least 2020 (Teck Resources Ltd., 2016, p. 20; 2017a, p. 39, 45; 2017b).

Nyrstar's Clarksville zinc smelter in Tennessee was thought to have not produced byproduct germanium concentrate in 2016 owing to the absence of zinc-concentrate feedstock from the Middle Tennessee mines. In December 2015, Nyrstar placed the Middle Tennessee mines on care-and-maintenance status owing primarily to the decline in the price of zinc during the second half of 2015. Refined zinc production at the Clarksville smelter in 2016 decreased by 10% from that of 2015 to 111,000 t owing to the processing of lower grade zinc concentrates following the suspension of the Middle Tennessee mines. In September 2016, Nyrstar announced actions for the restart of the mine complex. Ore production was projected to commence during the first quarter of 2017, and mill processing operations were to commence during the second quarter of 2017 (Nyrstar NV, 2016a, c, 2017).

Secondary germanium metal was recovered by secondary processors from end-of-life products, such as decommissioned military vehicles and thermal weapons sights.

Consumption

The USGS estimated that domestic consumption of germanium metal (including metal content of compounds) was about 30,000 kg in 2016 (table 1). A major domestic consumer of germanium reported that demand for germanium tetrachloride used for infrared optics increased in 2016 from that in 2015 (Umicore s.a., 2017, p. 11, 23–24). Germanium-containing infrared optics were primarily for military use, and the commercial and personal markets for thermal-imaging devices that use germanium lenses has grown over the past few years. The major global end uses were fiber-optic systems, infrared optics, electronics and solar applications, polymerization catalysts, and other uses (such as phosphors, metallurgy, and chemotherapy).

Fiber-Optic Systems.—Germanium dioxide is used as a dopant (a substance added in small amounts) in the pure silica glass core of optical fibers to increase the refractive index, preventing signal loss while not absorbing light. Three producers in Japan (Fujikura Ltd.; Furukawa Electric Co., Ltd.; and Sumitomo Electric Industries, Ltd.) and Corning Inc. in the United States accounted for a substantial portion of global production of germanium-doped silica glass used in fiber-optic cable. In 2016, Corning reported that sales of its optical communications products increased slightly from those in 2015 owing partially to increased carrier network sales and increased sales of fiber-optic

cable and hardware for fiber-to-the-home installations in North America (Yi, 2013; Corning Inc., 2017, p. 28).

Infrared Optics.—Germanium was used in lenses and windows for infrared optical systems owing to its transparency to part of the infrared spectrum and to its high refractive index. FLIR Systems, Inc. (Wilsonville, OR), a leading domestic producer of infrared surveillance devices, reported a 5.9% increase in sales revenue in 2016 compared with that in 2015. This increase in revenue was primarily a result of its acquisition of Armasight, Inc. (San Francisco, CA) in June 2016 (FLIR Systems, Inc., 2017, p. 40–41).

Polymerization Catalysts.—Estimates indicated that consumption of germanium for PET outside the United States has been declining since 2011 owing to germanium price increases that led to substitutions for germanium. Producers have substituted lower cost antimony- and titanium-based products for germanium dioxide catalysts. The majority of germanium consumed for PET resin production took place in Japan, where the high brilliancy of the polymer is preferred for bottle applications.

Solar Cells.—Germanium-based solar cells were used in space-based applications and terrestrial installations. Umicore s.a. (Belgium), a leading germanium substrate producer, reported that orders of substrates for solar cells in space-based applications decreased in 2016 from that of 2015 (Umicore s.a., 2017, p. 11, 23–24).

5N Plus Semiconductors LLC (St. George, UT), a wholly owned subsidiary of 5N Plus Inc. (Canada), primarily produced germanium substrates for solar cells used in satellites. The company had the capability to produce germanium metal from germanium dioxide at its facility in Utah and recover germanium from industry-generated new scrap at other facilities.

Prices

Germanium is generally traded through long-term supply contracts among consumers, producers, and traders. Publicly available prices from Argus Media group – Argus Metals International are estimates of representative prices in trades being executed on a particular day and are compiled through recurring interviews with individual traders. Reported germanium metal (minimum 99.999% germanium) prices began the year at about \$1,250 per kilogram and decreased during the year to about \$900 per kilogram at yearend. Germanium metal prices averaged at about \$1,087 per kilogram for 2016 (fig. 1, table 3). Germanium dioxide prices began the year at about \$1,000 per kilogram, trended downward and ended the year at \$625 per kilogram. Germanium dioxide prices averaged at about \$831 per kilogram for 2016 (fig. 1, table 3).

Foreign Trade

According to the U.S. Census Bureau, imports for consumption of germanium metal (wrought, unwrought, and powder) decreased by 45% to 11,000 kg in 2016 from 20,100 kg in 2015 (tables 1, 2). Unwrought germanium metal imports decreased by 59% to 6,660 kg in 2016 compared with 16,200 kg in 2015 (table 2). Decreased imports from Belgium, China, and

Germany were partially offset by an increase in imports from Japan. A similar trend was seen in wrought germanium metal; decreased imports from Belgium, China, Germany, and the United Kingdom were partially offset by an increase in imports from Russia. Imports of germanium powder increased to 2,235 kg in 2016 from 899 kg in 2015. In 2016, China, Belgium, and Germany, in descending order of quantity, accounted for 86% of all types of germanium metal imported into the United States. The estimated germanium content of the germanium dioxide imported in 2016 was about 15,200 kg, a 6% increase compared with 14,300 kg in 2015 (table 1).

Domestic exports of germanium metal and articles thereof were estimated to be about 4,780 kg in 2016 based on trade data from the U.S. Census Bureau that were adjusted by the USGS to exclude low-value scrap. Belgium, Germany, Japan, Russia, and the United Kingdom accounted for the majority of germanium exported from the United States in 2016. The estimated germanium content of germanium dioxide exported from the United States in 2016 was less than 100 kg.

World Review

In 2016, world production of germanium recovered from zinc concentrates, coal fly ash, and recycled material was estimated to be about 126,000 kg (table 1). Scrap was estimated to have supplied about 30% of the world's total production of germanium. Owing to the high 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 old scrap, such as fiber-optic windows from decommissioned military vehicles or fiber-optic cables, has increased during the past decade. China accounted for the majority of global germanium production. 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, and coal ash in Russia.

As a byproduct metal, the supply of germanium was heavily reliant on zinc mine production, which decreased by 7% worldwide in 2016 from that in 2015. 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).

Australia.—In 2015, Nyrstar NV announced plans to upgrade production capacity at its zinc smelter in Hobart, Tasmania, Australia. The upgrades included construction of a side-leach plant that would enable the smelter to split base metals from minor metals and produce germanium and indium. The development phase of the project progressed in 2016 and is projected to be completed by yearend 2018 (Nyrstar NV, 2015, 2016b).

Belgium.—Umicore produced germanium metal, germanium tetrachloride for fiber optics, germanium substrates, and germanium optical products at its refinery and recycling plant in Olen. In 2016, the company reported decreased sales of substrates for solar cells used in satellites, finished optical devices containing germanium for infrared applications, and

germanium tetrachloride for use in fiber optics (Umicore s.a., 2017, p. 11, 23–24).

Canada.—The metallurgical complex operated by Teck in Trail, British Columbia, 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. In 2016, it was estimated that Canada exported about 20,000 kg of germanium contained in dioxide (Teck Cominco Ltd., 2008; Global Trade Information Services Inc., 2017a).

China.—China continued to be the leading global producer of germanium metal and germanium compounds, which were recovered from germanium-bearing coal ash and zinc ore. In 2016, an estimated 80,000 kg of germanium metal was produced in China. Germanium prices in China fell steadily throughout 2016. The drop in prices was attributed to an oversupply of germanium and reduced investment demand after the collapse of the Fanya Metal Exchange in 2015 (Metal-Pages, 2016b; Roskill's Letter from Japan, 2016).

Most of China's consumption of unwrought germanium in 2016 was used to produce specialized wafer and lens products in order to maximize profits during the decrease in metal prices (Shen, 2016). According to news sources, mines in China reduced their production and sales of germanium concentrates because of low prices. Production was also limited or suspended in some regions of China owing to stricter environmental protection requirements (Minor Metals Monthly, 2017a, p. 29–31). Yunnan Lincang Xinyuan Germanium Industrial Co., Ltd., China's leading private-sector germanium producer, reported decreasing profits since 2015; in October 2016, the company received a Government subsidy (equivalent to \$744,000) to finance the development of value-added germanium products (Metal-Pages, 2016b, c; Shen, 2016).

China exported 16,075 kg of unwrought and wrought germanium metal in 2016, a 48% increase from 10,870 kg in 2015, and imported 3,298 kg of metal in 2016, a 30% decrease compared with that of 2015 (Minor Metals Monthly, 2017b, p. 17–19).

China's State Reserve Bureau (SRB) was expected to purchase 30,000 kg of germanium for its national stockpile by March 2016 (30,000 kg was purchased in 2015), and analysts expected that China would continue to stockpile germanium during the next several years (Shen, 2015; Metal-Pages, 2016a). The Yunnan local government started bankruptcy proceedings for the Fanya Metal Exchange (FME) in late 2015 and Kunming police have seized FME assets and capital, which included about 70,000 t of nonferrous metals. The FME claimed it held 92 t of germanium in its warehouses before it shut down. It was thought that the germanium stocks previously held by FME could be acquired by China's SRB stockpiling program (Metal Bulletin, 2016; Roskill's Letter from Japan, 2016).

Russia.—During the past few years, Russia's germanium production was estimated to have remained stable. Exports in 2016 decreased by about 9% compared to those of 2015 (Global Trade Information Services Inc., 2017b). Germanium and Applications Ltd. 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 21,000 kilograms per year 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., 2014).

JSC Germanium operated an integrated refinery in Krasnoyarsk that processed concentrates, fly ash, and waste to produce germanium metal, compounds, and finished products. The company reported that it could produce germanium at a rate of about 20,000 kilograms per year, but it did not specify if that included the metal content of finished products, such as germanium lenses. JSC exported more than 80% of the germanium that it produced (JSC Germanium, 2016).

Outlook

Global demand for fiber-optic cable, led by the emerging Asian economies and Brazil, is likely to increase during the next several years. 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, increased substitution of specialty glass for pure germanium in infrared applications may continue to be attractive to some consumers. New applications for infrared products that use germanium lenses in commercial and industrial markets are expected to become more prevalent and represent a significant potential for consumption growth. Infrared cameras that are designed to be used with smartphones could become more appealing for commercial uses as prices decline and quality increases. These cameras typically use small quantities of germanium per unit, but the overall volume could be large based on the global proliferation of smartphones.

Germanium production will continue to be reliant on the zinc market. 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. In China, germanium producers are expected to continue to expand to downstream products and manufacture finished infrared products for export. Overall, the germanium market is expected to remain relatively balanced during the next several years owing to limited sources of supply and modest increases in consumption. This balance could change if some of the germanium stocks held in China begin to enter the global market; however, it is believed that the SRB would continue purchasing germanium through 2017 (Pugsley, 2014).

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 $\begin{tabular}{ll} TABLE 1 \\ SALIENT GERMANIUM STATISTICS \end{tabular} \\$

(Kilograms, unless otherwise specified)

		2012	2013	2014	2015	2016
United States:						
Refinery production ^e		W	W	W	W	W
Imports for consumption:						
Germanium metal ²		37,500	34,200 ^r	23,700	20,100	11,000
Germanium dioxide ^{e, 3}		11,000	11,400	12,500	14,300	15,200
Exports, germanium metal ^{e, 4}		15,300	12,500	12,000	5,000	4,780
Consumption, germanium metal ^{e, 5}		38,000	38,000	32,000	34,000	30,000
Price, average:						
Germanium metal ⁶ dollars pe	r kilogram	1,464	1,778	1,918	1,792	1,087
Germanium dioxide ⁷	do.	1,179	1,307	1,291	1,211	831
Stocks, December 31, U.S. Government ⁸		16,400	16,400	13,400	13,400	13,400
World, refinery production: ^e						
China	.	105,000	110,000	98,000 ^r	100,000 r	80,000
Russia		5,000	5,000	6,000 ^r	6,000 r	6,000
Other ⁹		30,000	40,000	40,000	40,000	40,000
Total		140,000	155,000	144,000 ^r	146,000 ^r	126,000

^cEstimated. ^rRevised. do. Ditto. W Withheld to avoid disclosing company proprietary data; not included in "World, refinery production."

¹Table includes data available throgh May 23, 2017. Data are rounded to no more than three significant digits, except prices; may not add to totals shown.

²Includes Harmonized Tariff Schedule of the United States (HTS) codes 8112.92.6000, 8112.92.6500, 8112.99.1000.

³Includes HTS code 2825.60.000. Data have been adjusted to exclude low-value shipments, then multiplied by 69% to account for germanium content.

⁴Includes HTS codes 8112.92.6100, 8112.99.1000, 2825.60.0000. Data have been adjusted to exclude low-value shipments. Oxide data multiplied by 69% to account for germanium content.

⁵Estimated consumption of germanium contained in metal and germanium dioxide.

⁶Minimum 99.99% germanium. Source: Argus Media group – Argus Metals International.

⁷Minimum 99.99% germanium dioxide, approximately 69% metal content. Source: Argus Media group – Argus Metals International.

⁸Defense Logistics Agency Strategic Materials. Data are uncommitted germanium metal only.

⁹Includes Belgium, Canada, Germany, and other countires.

 ${\bf TABLE~2}$ U.S. IMPORTS FOR CONSUMPTION OF GERMANIUM METAL, BY COUNTRY OR LOCALITY $^{\rm I}$

(Kilograms and dollars)

	20	012	20	013	20	014	20	015	20	16
Country or locality	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value
Unwrought: ²			•		· · · · · · · · · · · · · · · · · · ·		•		<u>-</u>	
Belgium	5,280	8,010,000	2,250	3,720,000	7,010	13,100,000	5,220	8,280,000	1,560	2,070,000
Canada	1,660	93,900	2,360	1,020,000	503	62,000	3	8,040		
China	21,200	27,600,000	20,800	33,000,000	11,200	18,400,000	10,700	16,000,000	4,930	4,590,000
Germany	76	136,000	71	143,000	346	515,000	309	427,000	31	25,700
Hong Kong	582	596,000	193	368,000						
Russia	1,620	1,370,000	267	211,000	271	151,000	32	19,400		
Other (4 countries)	331	368,000	200	354,000	3	5,330	1	4,500	140	112,000
Total	30,800	38,100,000	26,100	38,800,000	19,300	32,200,000	16,200	24,700,000	6,660	6,800,000
Powder: ³										
Belgium	134	187,000	37	83,400	55	291,000	77	513,000	712	860,000
Canada	25	3,040			4	2,600				
China	557	732,000	3	3,000	8	32,000	57	53,100	618	620,000
Germany	210	303,000	114	222,000	471	951,000	480	822,000	639	868,000
Russia	263	441,000	406	661,000	305	458,000	217	283,000	263	282,000
United Kingdom					5	3,430	65	80,700	3	4,370
Other (4 countries)	3	7,540	10	8,910	1	5,000	3	3,980		
Total	1,190	1,670,000	570	978,000	849	1,740,000	899	1,760,000	2,240	2,630,000
Wrought: ⁴										
Belgium	1,080	971,000	3,250	2,990,000	549	948,000	300	461,000	66	105,000
Canada	674	936,000	85	117,000	3	36,300				
China	1,910	2,380,000	2,360	3,920,000	1,910	3,380,000	1,480	2,400,000	684	881,000
Germany	244	403,000	156	471,000	364	802,000	512	1,060,000	226	328,000
Romania							153	292,000	277	615,000
Russia	1,610	2,400,000	1,650	2,210,000	705	1,110,000	343	500,000	866	1,300,000
United Kingdom					1	4,000	108	33,600	20	35,200
Other (8 countries)	1	6,480	1	18,200	9	42,400	64	109,000	9	10,500
Total	5,510	7,100,000	7,500	9,730,000	3,540	6,330,000	2,960	4,850,000	2,150	3,280,000

⁻⁻ Zero.

Source: U.S. Census Bureau.

TABLE 3 ANNUAL AVERAGE PRICES

(Dollars per kilogram)

-	Germanium metal	Germanium dioxide		
	(minimum 99.99% purity)	(minimum 99.99% purity)		
2007	1,106	767		
2008	1,456	948		
2009	1,054	677		
2010	953	575		
2011	1,539	1,218		
2012	1,464	1,179		
2013	1,778 ^r	1,307		
2014	1,918	1,291		
2015	1,792	1,211		
2016	1,087	831		
Average	1,415 ^r	1,000		

Source: Argus Media group – Argus Metals International.

¹Table includes data available throgh May 23, 2017. Data are rounded to no more than three significant digits; may not add to totals shown.

²Includes Harmonized Tariff Schedule of the United States (HTS) code 8112.92.6000.

³Includes HTS code 8112.92.6500.

⁴Includes HTS code 8112.99.1000.

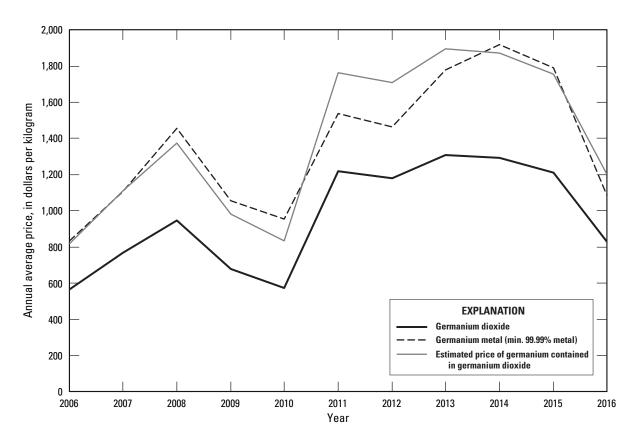


Figure 1. Average annual prices for germanium metal and germanium dioxide from 2006 through 2016. Source: Argus Media group – Argus Metals International.