

# 2006 Minerals Yearbook

## **GERMANIUM**

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#### Domestic survey data and table were prepared by Maria Arguelles, statistical assistant.

In 2006, germanium was recovered from zinc concentrates at two zinc mines and produced at two refineries in the United States. Germanium-bearing concentrates were produced at the two domestic zinc mines in Alaska and Washington, both operated by Teck Cominco Limited. These concentrates were then shipped to Canada for processing. The two U.S. refineries were located in New York and Oklahoma, where germanium was produced from manufacturers' scrap, post consumer scrap, and imported germanium compounds were processed.

The U.S. Geological Survey (USGS) estimated domestic germanium reserves, factored from zinc reserves, to be 450,000 kilograms (kg). Data for worldwide reserves were not available. Worldwide germanium resources were associated with zinc and lead-zinc-copper sulfide ores. Germanium was also recovered to a lesser extent from coal ash and cobalt-copper ores.

Germanium is a hard, brittle semimetal that first was used about one-half a century ago as a semiconductor material in radar units and as the material for the first transistors. Today, it is used principally as a polymerization catalyst for polyethylene terephthalate (PET), a commercially important plastic; a component of glass in telecommunications fiber optics; in infrared night-vision devices; and as a semiconductor and substrate in electronics circuitry.

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

As a strategic and critical material, germanium was included in the National Defense Stockpile (NDS) in 1984. All the material purchased for the stockpile was zone-refined polycrystalline germanium metal. Under Basic Ordering Agreement (BOA) DLA-Germanium-002, germanium was offered for sale on the fourth Monday of each month. In July 2006, the Defense National Stockpile Center (DNSC) issued a new BOA solicitation for germanium, DLA-Germanium-003. Postings for sales were conducted each Thursday on the DNSC Web site and price quotes from prequalified BOA holders were due the following Wednesday.

According to the Defense Logistics Agency (DLA), sales began 2006 at \$686 per kilogram and ended the year at \$970 per kilogram. The DLA reported that sales for calendar year 2006 were 4,579 kg compared with 4,512 kg in 2005 and that, as of December 31, 2006, the NDS inventory of germanium metal was 23,660 kg, all of which has been authorized for sale (Defense Logistics Agency, 2006a). The DLA was authorized to sell up to 8,000 kg during fiscal year 2007 (Defense Logistics Agency, 2006b).

#### **Production**

Domestic refinery production for germanium was estimated by the USGS based on data provided by North American producers. The USGS estimated that U.S. refinery production of germanium from fly ash, imported primary material and germanium compounds, and new scrap increased in 2006 to 4,600 kg from 4,500 kg in 2005. Production of refined germanium in 2004 and preceding years was revised significantly downward to avoid counting material imported in chemical form and directly consumed or consumed in the production of other germanium compounds.

Teck Cominco Limited (Vancouver, British Columbia, Canada) produced germanium-containing zinc concentrates at its Red Dog zinc-lead open pit mine in Alaska and its Pend Oreille zinc-lead underground mine in Washington State. Approximately 25% of zinc concentrate produced at Red Dog and 100% of all concentrate produced at Pend Oreille were shipped to the company's metallurgical complex in Trail, British Columbia, Canada. The zinc concentrates were then treated in roasters or pressure leach facilities to extract germanium and other coproducts (Teck Cominco Limited, 2006a, p. 8). A process involving the addition of shredded electronic waste as a supplemental feed to the normal furnace charge was developed and demonstrated in 2005. Germanium and other metals were fumed and integrated into the daily products made by Trail Operations (Teck Cominco Limited, 2006b, p. 23). In 2006, the company set a new record at its Trail facility and produced 33,200 kg of germanium (Teck Cominco Limited, 2007, p. 28).

In July 2003, Umicore Optical Materials USA Inc. (a subsidiary of Umicore NV/SA, Brussels, Belgium) acquired certain assets of EaglePicher Technologies, LLC's germanium operations based in Quapaw, OK, which remained the leading domestic producer of germanium in 2006. Umicore produced germanium from fly ash, germanium concentrates (typically containing 5% germanium or more), scrap, and imported germanium compounds. This facility also produced germaniumbased products used in fiber optics, infrared (IR) devices, and substrates for electronic devices such as their germanium arsenic selenium IR (GASIR) lenses used in far-infrared night vision systems. Sales of germanium optics reportedly increased from that of 2005, and sales of GASIR-based optical assemblies for automotive night-vision systems and nonautomotive applications increased steadily through the year (Umicore NV/SA, 2007, p. 5). Commercial deliveries of assemblies for nonautomotive applications started during the first quarter 2006. In April,

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Umicore acquired L-3 Communications Infrared Products (a division of L-3 Communications Corp., Dallas, TX) including intelligent property, equipment, and materials associated with chalcogenide infrared optical glass and lens production (Metal-Pages, 2006j).

Germanium Corporation of America (a subsidiary of Indium Corporation of America, Clinton, NY) produced germanium products including germanium dioxide, germanium metal, and germanium tetrachloride at its facility in Utica, NY.

AXT, Inc. (Fremont, CA), a major manufacturer of compound semiconductor substrates, started to sell germanium as well as other raw materials in the beginning of 2006. This likely gave the company a competitive advantage in the substrate marketplace. The raw materials were offered as a part of AXT's joint-venture operations with five companies in China (Metal-Pages, 2006a).

#### Consumption

The USGS estimated that domestic consumption of germanium increased to 38,500 kg in 2006 from 27,800 kg in 2005 owing to a continued growth in IR and fiber optic applications. Worldwide, the end-use pattern was estimated to be as follows: catalysts for polyethylene terephthalate (PET), 30%; infrared optics, 30%; fiber optics, 20%; electrical/solar applications, 15%; and other uses (such as phosphors, metallurgy, and chemotherapy), 5%. The domestic end-use pattern was significantly different, however, with infrared optics accounting for 40%; fiber optics, 30%; electronics/solar electrical applications, 20%; and other uses (phosphors, metallurgy, and chemotherapy), 10%. Germanium was not used in PET catalysts in the United States.

In the fiber optics sector, germanium continued to be used as a dopant (a substance added in small amounts to the pure silica glass core to increase its refractive index while not absorbing light) within the core of optical fibers allowing optical data transmission through fiber. Germanium lenses and windows are transparent to infrared radiation, which allows them to be used in infrared optical systems in the same way that ordinary glass lenses and windows are used in visible-light optical systems. These germanium-based optical systems have been used principally for military guidance and weapon-sighting applications, including satellite systems and personnel detection equipment for poor visibility environments. Germanium optical glass also was used for nonmilitary purposes in monitoring systems, night-vision applications for luxury vehicles, and surveillance equipment. U.S. car manufacturers have reported to be buying more germanium for infrared systems in luxury cars (Metal-Pages, 2006c).

Germanium was also used in a tarnish-proof sterling silver alloy, trademarked Argentium Sterling Silver, containing about 1.2% germanium. Argentium Sterling Silver was produced by Stern Leach Company (Attleboro, MA). The alloy is free from firescale when heated, remains unstained, and is stronger allowing for larger silver designs.

In the polymerization catalysts sector outside the United States, germanium consumption as a catalyst for PET production has remained stable.

Germanium-based devices have become well established for analog and digital functions. Silicon germanium (SiGe) enables manufacturers to produce smaller transistors with less electronic noise interference. Germanium-based transistors, referred to also as chips, are more energy efficient than traditional silicon-based chips, extending the life of the battery in wireless devices. Other benefits include more stability over a wider range of temperatures and the ability to operate at ultrahigh frequencies (IBM Research, 2007). The company developed a silicon-germanium chip that reportedly runs above 500 gigahertz (GHz) by chilling the chip to negative 451 °F. At room temperature, the chips operated nearly 350 GHz, and continued research conducted by IBM along with the Georgia Institute of Technology would enable IBM to explore performance barriers of silicon to faster, lower-energy chips (Metal-Pages, 2006d).

A new technique was developed by U.S. scientists called surfactant templating to create porous germanium. Porous materials have unique properties and are ideal as catalysts and sensors. More research is underway as the material could be used to make more efficient solar cells and chemical sensors (Metal-Pages, 2006h). In relation to solar cells, Mitsubishi Heavy Industries, Ltd. (Tokyo, Japan) conducted research on SiGe film contained in solar cells to further increase efficiency. The company expected in spring 2007 to market a microcrystalline tandem-type solar cell that increased powergeneration efficiency (Metal-Pages, 2006f).

Both the fiber optic market and the SiGe sector displayed an increase in activity mostly owing to fiber-to-the-home connections (FTTH). FTTH is a form of fiber-optic communication delivery in which the signal reaches the end user's living or office space. The number of U.S. homes receiving internet, video, and voice services over direct fiber-optic connections has also increased dramatically during the past years. According to data provided in April by the FTTH Council and the Telecommunications Industry Association, the number of optical fiber communities in the United States has risen to 936, a 43% increase from that of October 2005. In addition, there has been a 50% increase in homes which are fiber ready and a 107% increase in homes reportedly connected with fiber since October 2005 (Telecommunications Industry Association, 2006).

#### **Prices**

Free market prices for germanium dioxide, published by Metal Bulletin, increased from prices ranging from \$360 to \$430 per kilogram at the beginning of the year to \$620 to \$660 per kilogram by the end of 2006. Based on DNSC sales, the price of zone-refined germanium metal averaged \$839.11 per kilogram during 2006 (Defense Logistics Agency, 2006a).

#### Trade

According to the U.S. Census Bureau, imports of germanium (wrought, unwrought, and waste and scrap material) increased to approximately 24,100 kg in 2006 from 16,700 kg in 2005. Belgium, Germany, China, and Russia, in descending order of quantity, accounted for 94% of imports into the United States

in 2006 (table 1). In addition, the estimated germanium content of the germanium dioxide imported in 2006 was 19,500 kg compared with 11,800 kg in 2005. When metal imports and estimated metal content of germanium dioxide imports are added together, Canada accounted for 34.5%; Belgium, 29.6%; Germany, 13.5%; China, 12.1%; and Russia, 6.0% of imports of contained germanium metal into the United States.

Exports of germanium and articles thereof, including waste and scrap, were 63,000 kg in 2006 according to the U.S. Census Bureau. Low-value waste exported to Belgium accounted for about 76% exports of germanium from the United States in 2006. The estimated germanium content of germanium dioxide exported in 2006 was 651 kg. When metal exports and estimated metal content of germanium dioxide exports were added together, Belgium was the destination for 69.4%; Canada, 6.5%; China, 4.6%; Germany, 3.1%; and Vietnam, 3.1% of exports of contained germanium metal from the United States.

In May, Russia suspended import duties on raw materials containing germanium. According to Russian legislation, the zero tariff must remain in effect for 9 months, after which the Government can extend it for another 9 months, or indefinitely, or reintroduce it before the abolishment can be finalized (Metal-Pages, 2006g).

#### World Review

In 2006, the world's total estimated supply of germanium was 100 metric tons (t), including 4,600 kg released from the NDS. The recycling level remained about the same and supplied about 35 t of the world's total supply of germanium.

Beginning in 2001, there was a growing surplus of germanium owing to a major downturn in the fiber-optics market. By yearend 2003, supply and demand were in close balance followed by lower production and moderate demand growth in 2004, which resulted in a tight supply that continued through 2005. In 2006, production decreased while consumption strongly rose resulting in a deficit (Metal-Pages, 2006i).

In China, more than a dozen zinc smelters closed because of hazardous environmental conditions that began at the end of 2005 and continued through May 2006. These closures contributed to a decrease in production and an increase in prices.

#### Outlook

During recent years, it appears that an increasing amount of research and development has been conducted for several applications involving the usage of germanium. It continues to show potential across its applications as there is strong demand in various sectors.

A major growth area for germanium was in the IR optics area owing to increased interest for IR devices by the military, in security and surveillance equipment, and in the automobile market. Germanium-based semiconductors and other electronic uses for germanium also continue to show growth potential. Demand by the military and the defense industry could account

for a significant portion of germanium consumption in the future (Metal-Pages, 2006e).

The fiber optics industry continues to grow as the U.S. FTTH program aims to deliver fiber optic cables to every U.S. home. The estimated growth of the fiber optics market has been 8% per year since 2004 from developing countries (Metal-Pages, 2006b).

While there was a deficit owing to reduced germanium production and increased consumption in 2006, supply and demand will probably balance out as output increases and more recycling takes place in 2007.

#### **References Cited**

- Defense Logistics Agency, 2006a, Correction annual materials plan for FY 2007: Fort Belvoir, VA, Defense Logistics Agency news release, October 3, 2 p.
- Defense Logistics Agency, 2006b, Stockpile accepts germanium bids: Fort Belvoir, VA, Defense Logistics Agency news release, June 6, 1 p.
- IBM Research, 2007, Silicon germanium fact sheet: Armonk, NY, IBM Corporation, 2 p. (Accessed March 30, 2007, at http:// domino.research.ibm.com/comm/pr.nsf/pages/rsc.sige.html.)
- Metal-Pages, 2006a, AXT starts selling raw materials: Teddington, United Kingdom, Metal-Pages, January 26, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Metal-Pages, 2006b, Germanium dioxide climbs: Teddington, United Kingdom, Metal-Pages, March 3, 1 p. (Accessed March 21, 2007, via http:// www.metal-pages.com.)
- Metal-Pages, 2006c, Germanium looking firmer: Teddington, United Kingdom, Metal-Pages, April 21, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Metal-Pages, 2006d, IBM develops world's fastest frozen chip: Teddington, United Kingdom, Metal-Pages, June 21, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Metal-Pages, 2006e, Market Roundup: Teddington, United Kingdom, Metal-Pages, January 13, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Metal-Pages, 2006f, Mitsubishi to start selling tandem-type solar cell: Teddington, United Kingdom, Metal-Pages, November 9, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Metal-Pages, 2006g, Russia cuts import duties on Ge raw materials: Teddington, United Kingdom, Metal-Pages, May 30, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Metal-Pages, 2006h, Scientists produce porous germanium: Teddington, United Kingdom, Metal-Pages, July 12, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Metal-Pages, 2006i, Semi-conductor industry taking toll on germanium: Teddington, United Kingdom, Metal-Pages, September 11, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Metal-Pages, 2006j, Umicore see Q1 revenue rise 11%: Teddington, United Kingdom, Metal-Pages, April 27, 1 p. (Accessed March 21, 2007, via http://www.metal-pages.com.)
- Teck Cominco Limited, 2006a, 2005 annual information form: Vancouver, British Columbia, Canada, Teck Cominco Limited, March 1, 45 p.
- Teck Cominco Limited, 2006b, The Teck Cominco Citizen December 2006: Vancouver, British Columbia, Canada, Teck Cominco Limited, 27 p.
- Teck Cominco Limited, 2007, Annual report 2006: Vancouver, British Columbia, Canada, Teck Cominco Limited, 117 p.
- Telecommunications Industry Association, 2006, FTTH reaches 936 communities; 280 added since October 2005: Washington, DC, Telecommunications Industry Association news release, April 26, 2 p. (Accessed March 21, 2007, at http://www.tiaonline.org/business/media/press\_releases/2006/JointPR06-03.cfm.)
- Umicore NV/SA, 2007, 2006 Results: Brussels, Belgium, Umicore NV/SA news release, February 15, 24 p.

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#### Other

#### **U.S.** Geological Survey Publications

Gallium, Germanium, and Indium. Ch. in United States Mineral Resources, Professional Paper 820, 1973. Germanium. Ch. in Mineral Commodity Summaries, annual. Germanium. Ch. in Mineral Facts and Problems, U.S. Bureau of Mines Bulletin 675, 1985.

 $\label{eq:table 1} \textbf{U.S. IMPORTS OF GERMANIUM, BY CLASS AND COUNTRY}^{1,2}$ 

	2005		2006	
	Gross weight		Gross weight	
Class and country	(kilograms)	Value	(kilograms)	Value
Wrought, unwrought, waste, and scrap:				
Belgium	9,060	\$4,930,000	11,400	\$5,900,000
Canada	282	191,000	426	354,000
China	3,110	2,080,000	3,770	2,770,000
Germany	2,300	2,350,000	4,810	5,330,000
Hong Kong			595	405,000
India	184	134,000		
Israel	16	17,700	7	6,330
Japan	45	32,100	254	168,000
Russia	1,740	1,490,000	2,610	2,870,000
United Kingdom	1	5,810	19	27,100
Other			137	116,000
Total	16,700	11,200,000	24,100	17,900,000

<sup>--</sup> Zero.

Source: U.S. Census Bureau.

 $<sup>^{1}\</sup>mbox{Data}$  are rounded to no more than three significant digits; may not add to totals shown.

<sup>&</sup>lt;sup>2</sup>Does not include germanium dioxide imports.