GERMANIUM

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

In 2002, the domestic germanium industry consisted of two zinc mines and two refineries. The zinc-mining operations in Alaska and Tennessee supplied byproduct germanium concentrates for export. The two refineries operated in Oklahoma and New York. The refineries processed manufacturers' scrap, imported semirefined materials, and some old postconsumer scrap.

Domestic refinery production and consumption for germanium are estimated by the U.S. Geological Survey (USGS) on the basis of data provided by North American producers. Domestic refinery production in 2002 is estimated to have decreased considerably, and U.S. consumption of germanium is estimated to have fallen during this period also.

The USGS estimated domestic germanium reserves to be 400,000 kilograms (kg), equivalent to about 25 years of domestic consumption at the 2002 rate; figures for worldwide reserves were not available. Worldwide, germanium resources are associated with zinc and lead-zinc-copper sulfide ores. Germanium is also recovered to a lesser extent from coal ash and cobalt-copper ores.

Legislation and Government Programs

As a strategic and critical material, germanium was included in the National Defense Stockpile (NDS) in 1984. In 1995, the Defense Logistics Agency (DLA), which maintains the NDS, made plans to sell germanium at a rate of 4,000 kilograms per year (kg/yr) through 2005. This proposed rate was increased to 6,000 kg/yr in 1997 and to 8,000 kg/yr in 1998. All the material offered is zone-refined polycrystalline germanium metal. The amount designated for annual sales is a significant portion of the domestic and world market. In most years, however, less than the amount available for sale has been sold (U.S. Department of Defense, 2003).

The DLA price has not only become a good indicator of the market value of germanium, but is also a factor in determining that value. Sales began in 2002 at just more than \$900 per kilogram and fell gradually to \$820 per kilogram by the end of September. In October, prices began to fall drastically, ending the year at \$461 per kilogram (Defense National Stockpile Center, 2003). After strong sales of 5,729 kg in 2001, the DLA recorded a disposal of only 681 kg of germanium metal, far below the authorized amount for 2002.

As of March 31, 2003, the NDS inventory of germanium

metal was 41,460 kg—all of which has been authorized for sale. Germanium is offered for sale on the fourth Monday of each month, and the DLA is authorized to sell up to 8,000 kg during fiscal year 2003 (American Metal Market, 2003).

Production

Teck Cominco Limited produces a germanium-containing zinc concentrate at its Red Dog Mine in Alaska. This concentrate is shipped to Trail, British Columbia, Canada, for smelting, refining, and germanium extraction. In August 2002, the milestone of 10 million metric tons (Mt) of concentrate shipped from Alaska was passed (Teck Cominco Limited, 2002b).

The USGS estimated that U.S. refinery production of germanium from primary and semirefined materials in 2002 was 12,000 kg, considerably less than the 20,000 kg produced in 2001. Specialty Materials Group of Eagle-Picher Technologies, LLC (EPT) in Quapaw, OK, remained the largest domestic producer in 2002, producing germanium from reprocessed scrap, fly ash, germanium concentrates (typically containing 5% germanium or more), and semirefined germanium materials. In 2001, EPT expanded its Oklahoma plant, which doubled its production capacity of germanium tetrachloride in response to growing demand expected in the fiber optics industry.

Indium Corporation of America (NY) produced germanium products under its newly formed subsidiary Germanium Corporation of America with facilities purchased from Cabot Corporation.

Pasminco Limited (Australia), the owner of the zinc refinery at Clarksville, TN, went into receivership in September 2001. The company continues to produce germanium-rich residues as a byproduct of processing zinc ores from its Gordonsville Mine. Pasminco has announced the planned closing of the Gordonsville Mine for June 2003 (Pasminco Limited, 2002b§¹). Consequently, the 300,000 metric tons (t) of germanium ore reserves at the mine will not be recovered unless the mine reopens. The Clarksville refinery will continue to operate, but without germanium-rich concentrates from the Gordonsville Mine as feed for the 20-t-capacity high-grade zinc residues plant (Pasminco Limited, 2002a§).

Pasminco has continued the established practice of shipping these residues to the optical materials unit of n.v. Umicore, s.a. (previously named Union Minière, s.a.) in Belgium for germanium recovery and refining. In February 2002, Umicore began production from a secondary germanium tetrachloride facility in North Carolina (Umicore, s.a., 2002b).

At the beginning of 2002, the Advanced Materials Group of Umicore, s.a. announced collaboration with Silicon Genesis

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¹References that include a section mark (§) are found in the Internet References Cited section.

Corporation (CA) to produce thick silicon-on-insulator (SOI) wafers. The initial operation will have an installed capacity of 50,000 wafers per year, which will form the base for development of advanced heterostructure materials including germanium. Both partners will market these SOI wafers (Umicore, s.a., 2002a).

Consumption

The USGS estimates that domestic consumption of germanium in 2002 was approximately 15,000 kg. The world use pattern was estimated to be as follows: polymerization catalysts, 35%; infrared optics, 25%; fiber optics, 20%; electrical/solar applications, 12%; and other uses (as phosphors, in metallurgy, and in chemotherapy), 8%. Both world and domestic use patterns have undergone drastic changes during the past year with the strong downturn in the telecommunications industry. The domestic use pattern was significantly different from worldwide use owing to the very small amount of germanium used in manufacturing PET in the United States.

In the fiber optics sector, germanium was used as a dopant (substance added in small amounts to a pure semiconductor material to alter its conductive properties for use in transistors and diodes) within the core of optical fiber used by the telecommunications industry. Because germanium lenses and windows are transparent to infrared radiation, they can be used in infrared optical systems in the same ways 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. Germanium glass was also used for non-military purposes in surveillance, night vision, and monitoring systems. It has been making in-roads into a wide range of fields, including satellite systems and personnel detection in poor visibility environments.

In the polymerization catalysts sector, PET consumption weakened primarily owing to economic conditions in the Far East. New types of materials are expected to replace the use of relatively expensive germanium catalyst and to reduce its overall growth for this end use.

Infrared equipment use by the military and civilian security forces increased following the terrorist events of September 11, 2001, with U.S. military operations in Afghanistan, and in anticipation of a conflict in Iraq. Although the consumption of germanium is not as high as several years ago, these increased security applications may have helped to slow a decline in demand.

A significant factor expected to influence germanium consumption in the early 21st century involves satellite communication systems. Satellite launch delays of the Teledesic Project, which is to be a large satellite-based communications system, resulted in a decline in solar cell manufacture. This project, if restarted, would require about 12,000 kg of germanium for solar cells (Mining Journal, 2000). The decline in consumption for solar cell applications was highlighted by the bankruptcy of Tecstar, manufacturer of the gallium arsenide on germanium cells for the Iridium Satellite LLC satellite constellation, in January 2002 (SpaceDaily, 2002§).

The use of germanium as a dopant in optical fibers declined

sharply in 2002 but is expected to continue to grow with a recovery of the telecommunications industry because metropolitan and fiber-to-home access is still underdeveloped.

Two automobile manufacturers have incorporated germanium-based night vision systems in limited editions of their product lines. At least one automotive manufacturer has announced a similar system for trucks and buses (Bendix Commercial Vehicle Systems LLC, 2002). These night vision systems are finding an additional application as fire departments improve their systems to include the use of germanium thermal imaging to detect hot spots, team members, and endangered individuals in smoky environments (Hansen, 2001).

Several manufacturers have begun production of silicon-germanium (SiGe) chips. During 2002, TriQuint Semiconductor, Inc. (OR) took over the design, development, marketing, and sales of certain standard and custom International Business Machines Corporation (IBM) semiconductor products used in wireless phones and other communications applications. The IBM products being transferred to TriQuint are all based on SiGe process technology (TriQuint Semiconductor, Inc., 2002§).

A company in New Jersey has been licensed to produce a sterling alloy containing 1.2% germanium. This new alloy, although not tarnish-free, has much better tarnish resistance than standard sterling and any faint tarnish that develops can easily be removed with ordinary water and a cellulose sponge. The new alloy is firestain resistant and, therefore, will represent a cost saving on finishing with no need to strip or plate over firestain (Herman, 2002§).

Prices

Throughout the 1981-95 period, germanium producers significantly discounted prices in response to competition from imported materials. In 1995 and 1996, however, producer prices for zone refined metal reportedly reached \$1,375 and \$2,000 per kilogram respectively; germanium dioxide producer prices rose to \$880 and \$1,300 per kilogram, respectively, during the same period.

In 1997, the producer prices fell back to \$1,475 per kilogram for the metal and \$950 per kilogram for the dioxide. In 1998, producer prices increased again to \$1,700 per kilogram for the metal and \$1,100 per kilogram for the dioxide. In 1999, the prices were reduced to \$1,400 and \$900 per kilogram, respectively, owing to sluggish demand. In 2000, prices continued to fall, reaching \$1,250 and \$800 per kilogram, respectively, mainly owing to plentiful supply rather than lack of demand. In 2001, prices again were lower, falling to \$890 per kilogram for the metal and \$575 per kilogram for the dioxide; dioxide prices reflected the ready availability of material from China.

Projections of price declines early in 2002 materialized as the fiber optic industry failed to recover, as exemplified by major players—WorldCom, Inc. and Nortel Networks Corporation (Metal Bulletin, 2002b). Inventories of germanium metal remained fairly low, as the decline begun in July 2001 continued dramatically through November 2002, when the price bottomed at approximately \$450 per kilogram. Free market prices for germanium dioxide, published by Metal Bulletin, began 2002 in

the \$620 to \$660 per kilogram range and ended the year in the \$250 to \$350 per kilogram range.

Trade

In 2002, the reported germanium content of imports was approximately 13,100 kg compared with 8,240 kg in 2001. Taiwan, Belgium, China, and Russia, in descending order of shipments, accounted for approximately 84% of U.S. germanium imports in 2002, based on trade data from the U.S. Census Bureau (table 1). Taiwan alone accounted for almost 43% of these imports in December 2002, according to Census trade statistics. Germanium export data are not available.

World Review

In 2002, world refinery production of primary germanium was estimated to be less than 50 t, a decrease of almost 30% from that of 2001. Recycling supplied 30 t of germanium worldwide, about the same as in 2001. The world total market supply was about 80 t in 2002, including only about 0.7 t released from the NDS, as producers and consumers reduced their internal stockpiles by about 10 t.

Belgium.—Umicore's Electro-optic Materials Unit continued delivery of germanium substrates at 2001 levels as part of a research contract with Estec, the research and technology center of the European Space Agency. The research contract has been developing germanium substrates for use in high-efficiency solar cells for satellite communication (Umicore, s.a., 2003§). Modern solar cells consist of a number of thin layers of gallium arsenide and aluminum-indium-gallium phosphide deposited on a germanium substrate. The next generation of solar cells will have a higher conversion efficiency and thinner layers that will require a higher grade germanium substrate (American Metal Market, 2001).

Umicore customers reduced their orders by more than the overall decline in demand for fiber optic cables, which might suggest they were using most of the germanium tetrachloride they already held in stock. This stock consumption amplified the market drop with Umicore's deliveries down from 2001 levels by more than 50% (Umicore, s.a., 2003). However, Umicore was able to record significant market share gains in these difficult circumstances, and good levels of germanium dioxide (GeO₂) deliveries alleviated the situation with germanium tetrachloride to a certain extent (Mining Journal, 2002).

Canada.—Teck Cominco continued development of the Pend Oreille lead-zinc deposit in Washington State (USA). The deposit contains 5.7 Mt of 7.7% zinc and 1.4% lead (Teck Cominco Limited, 2003). Concentrate with recoverable germanium will be sent to the Trail smelter in British Columbia, Canada, when operations start up in early 2004 (Teck Cominco Limited, 2002a).

China.—Of China's four germanium recovery plants, Chihong Zinc and Germanium Co. Ltd. is expected to upgrade its germanium output capacity to 20 metric tons per year (t/yr) by 2005 (China Metal Market, 2002).

Congo (*Kinshasa*).—The production of large reserves of germanium from the Big Hill slag pile in Congo (Kinshasa)

was questioned in a United Nations report in mid-2002 (Gjone, 2002§). Estimates indicate that approximately 3,000 t of germanium-containing material exists within this reserve, enough to supply 20% of the world's germanium dioxide needs for the next 30 years. The germanium-enriched material is planned for processing at a refinery in Kokkola, Finland, owned by OM Group, Inc. (Metal Bulletin, 2002a).

Germany/France.—PPM Pure Metals GMBH, a division of Metaleurop SA, received GeO₂ from the Metaleurop zinc smelter at Noyelles-Gaudalt in France. However, it was announced that this smelter would no longer process the primary ores and that the approximately 50 metric tons per year (t/yr) of indium and 7 t/yr of germanium would no longer be recovered.

Japan.—By midyear 2002, the average per-kilogram value of GeO₂ from China had fallen by 20% since the beginning of the year. Germanium metal unit values of imports from China had fallen by 12% (Roskill's Letter from Japan, 2003).

Yearend figures for Japan showed imports of GeO₂ at 42.7 t, down by 8% compared with those of 2001, and imports of germanium at 7.0 t, up by 3% compared with those of 2001.

The largest end use of germanium in Japan—the production of PET—remained at the 2001 levels, but some substitution of titanium oxide had been made for GeO₂ as the catalyst. As in Europe and the United States, demand for germanium tetrachloride dopants in optical fibers fell in Japan (Roskill's Letter from Japan, 2002).

Namibia.—ZincOx Resources plc announced a total tonnage of 2.9 Mt at its Tsumeb slag project. Check analyses at various laboratories indicate a germanium fume grade of 183 parts per million. ZincOx expects to recover 94% of the germanium from the fumes using Ausmelt technology, as well as additional values of gallium, indium, and zinc. Work continues on confirmation of reserves, acquisition of bulk samples, and metallurgical testwork (ZincOx Resources plc, 2002§).

Russia.—Recovery of germanium from Sakhalin coal ash provided an internal source for Federal State Unitary Enterprise "Germanium" to manufacture products at Krasnovarsk.

Current Research and Technology

Germanium continues to be used for thermal imaging in night vision systems using infrared rays. The germanium lens focuses the infrared rays from the observed object to a detector. All objects emit heat to some degree, but humans, animals, and moving vehicles are quite visible in the infrared spectrum because of the large contrast of emission from the object compared to its background. The night vision segment of the surveillance market is expected to grow from \$560 million in 1999 to \$750 million by 2004 (Hindus, 2000).

New applications using germanium alloys under development during 2002 included silicon-germanium semiconductor chips substituting for gallium arsenide in wireless telecommunications; a new sterling silver alloy that is tarnish resistant; and a new catalyst that combines germanium, oxygen, and silicon. The catalyst facilitates the breakdown of heavy oil into fuel and raw materials. The resulting fuel mixture has a higher octane number and is more efficient at turning oil into light hydrocarbons. Therefore, it is less likely to detonate prematurely in engines (Nature Science Update, 2002§).

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SiGe technology is poised for growth. SiGe chips combine the high-speed properties of germanium with the low cost, well-established production techniques of the silicon-chip industry. Most semiconductor technologies that use more than one material are complicated because of the physical and chemical differences between the components. Because silicon and germanium are compatible, SiGe processing can be relatively simple.

IBM announced that it has produced a prototype integrated circuit able to function at 110 gigahertz using its SiGe transistor. This transistor operates at almost twice the speed and with one-half the power consumption of traditional silicon transistors. This reduced power consumption will remove previous limitations imposed by heat buildup (Fowler-Child, 2002).

SiGe has been found to close the gap between high-volume silicon electronics and the high-performance III-V radio frequency electronics, such as gallium arsenide. Advances in device processing have been achieved over the past 10 years with maximum frequency values for SiGe heterojunction bipolar transistors increasing almost by an order of magnitude. Paralleling this development have been advances in SiGe heterostructure field effect transistors, where carrier mobilities are far greater than those of silicon-based devices (Hackbarth and others, 2002).

Toyobo Co., Ltd. developed a PET catalyst, which according to company representatives, is superior to existing catalysts. Most PET catalyst technology is currently based on the use of antimony, which along with the heavy metals, is now under regulatory pressure. Alternatives, such as germanium, are more expensive, or like titanium, do not produce PET with the clarity of the new aluminum-based catalyst that Toyobo is developing (Metal-Pages, 2003§).

Outlook

Demand will remain weak with a continued oversupply of both germanium metal and oxide. Higher recycling rates and declining demand as a catalyst in the production of PET plastic bottles will cause germanium oxide stocks to increase. Closure of zinc mines in Australia, Canada, and the United States, as well as smelting facilities in Europe, will result in lower output of byproduct germanium in the short term. This reduced supply will tend to offset the short-term reduction in demand.

Although the largest use of germanium in 2001 for optical fiber has declined considerably, a recovery in the telecommunications sector in fiber optics for the metropolitan and fiber-to-home consumption would mean a strong surge in demand for germanium. There is still significant strength and growth in the infrared optics area and also growth in the sterling alloy and in the thin film application for DVDs. Prices, therefore, can be expected to remain stable rather than continue to decline.

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

	2001		2002	
	Gross weight		Gross weight	
Class and country	(kilograms)	Value	(kilograms)	Value
Wrought, unwrought, waste, and scrap:				
Bangladesh	3	\$4,510		
Belgium	2,960	3,550,000	2,720	\$3,210,000
Bermuda	2	3,630		
Canada	1	2,740	712	313,000
China	3,470	2,450,000	1,780	815,000
France			15	2,480
Germany	701	940,000	865	933,000
Israel	69	83,900	96	101,000
Netherlands			2	4,860
Russia	905	613,000	927	741,000
Taiwan			5,630	37,200
Ukraine			176	96,500
United Kingdom	131	196,000	222	151,000
Total	8,240	7,840,000	13,100	6,410,000

⁻⁻ Zero.

Source: U.S. Census Bureau.

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¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Does not include germanium dioxide imports.