



Mineral Commodity Profiles

Germanium

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MINERAL COMMODITY PROFILES

Germanium

Overview

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 transistor was 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 (IR) night vision devices; and as a semiconductor and substrate in electronics circuitry.

Most germanium is recovered as a byproduct of zinc smelting, although it also has been recovered at some copper smelters and from the fly ash of coal-burning industrial powerplants. It is a highly dispersed element, associated primarily with base-metal sulfide ores. In the United States, germanium is recovered from zinc smelter residues and manufacturing scrap and is refined by two companies at four germanium refineries. One of the four refineries is dedicated to processing scrap. In 2000, producers sold zone-refined (high-purity) germanium at about \$1,250 per kilogram and electronic-grade germanium dioxide (GeO₂) at \$800 per kilogram. Domestic refined production was valued at \$22 million.

Germanium is a critical component in highly technical devices and processes. It is likely to remain in demand in the future at levels at least as high as those of 2000. U.S. resources of germanium are probably adequate to meet domestic needs for several decades.

Historical Background

In 1864, John Newlands postulated the existence of an element that would be intermediate between silicon and tin in his scheme of elemental octaves. In 1871, salient properties of the undiscovered element were predicted by Dmitri Mendeleev, who called it ekasilicon (beyond silicon) (Greenwood and Earnshaw, 1998, p. 367). In 1886, the element was isolated from the silver sulfide mineral argyrodite and described by Clemens Winkler (1886). He named it germanium, after his native country.

More than half a century elapsed after the isolation of germanium before its first commercial use was developed. During World War II, it came to be used in the newly invented radar devices as a solid-state signal-processing rectifier diode. The diodes used in radar in the early years of the war were subject to burnout by stray voltages. A tin-doped germanium diode developed in the United States proved 10 times more resistant to burnout than the standard diodes. Immediately after the war, the use of germanium expanded quickly. In the U.S. Bureau of Mines (BOM) Minerals Yearbook for 1946, it was remarked that domestic production of germanium from cadmium fume, which is a byproduct of the sintering of zinc concentrates at smelters, had reached a level of several hundred pounds per year for the first time (U.S. Bureau of Mines, 1937-1995). (Because of the paucity of data about the consumption of germanium in other countries, the rest of this section refers to activity in the United States, which, along with Japan, has been a pace setter in applications development.)

By 1948, large numbers of germanium diodes were being used in electrical test equipment, electronic computers, telephone circuits, and the detector circuits of television sets. Large electronic computers employed several thousand diodes, and telephone exchange circuitry was believed to be a big potential user, which eventually would require perhaps hundreds of thousand of diode units. By that time, germanium was also being used in special optical glasses, in which its high refractive index was advantageous, and in phosphors and film resistors (germanium

metal on ceramic substrates). Most important in that year, in retrospect, was the statement by Bell Telephone Laboratories that it had developed a solid state triode or “transistor.” Similar in size to the diode, the transistor could be employed as an oscillator or amplifier or for other purposes for which vacuum tubes were ordinarily used. The advantages of the transistor compared with the vacuum tube were reported as wide frequency range, small size, lightness, longevity, low current requirements, and freedom from the low-frequency hum inherent in vacuum tubes (U.S. Bureau of Mines, 1937-1995).

Demand for germanium grew at a very fast rate in the 1950s; by 1956, U.S. estimated consumption had risen to 10,000 kilograms (kg), and by 1960 it had reached its peak at more than 45,000 kg. The wider use of germanium semiconductor devices was made possible by advances in the zone-refining technique, which had been invented in 1951 specifically for producing ultrapure germanium, and in the ability to grow large single crystals of germanium. Refinery production rose along with demand but did not quite keep pace, and the shortfall was filled with imported material. Electronic uses dominated the germanium market from the 1940s through the mid-1970s. The absolute size of the germanium market, however, lagged behind the explosive growth in use of electronic devices of all kinds because germanium was being supplanted in many circuits by silicon. Silicon was cheaper as a material and, more importantly, lent itself much more readily to the new techniques developed for the manufacture of large-scale (LS) and very-large-scale (VLS) integrated circuits. Germanium was favored for certain high-frequency and high-power devices, but silicon had supplanted it in most microelectronic components by the end of the 1970s.

As early as the 1940s, the ability of germanium metal and germanium-containing glasses to transmit near-IR radiation was recognized as a critical property for use in night vision devices of the passive variety—those that use heat radiated by objects to view the objects. Demand for such devices for military purposes grew steadily and, by the late 1970s, had displaced electronics as the principal end use for germanium. IR use remained dominant until the early to mid-1990s when use in fiber optic transmission lines, which had been growing since the late 1970s, became the principal end use.

At least as early as the mid-1960s, single crystals of doped germanium were being used in detectors for gamma and x radiation. This small but still significant end use remained a steady market over the years and by the mid-1990s, when data on the market were last published, still accounted for about 10 percent of domestic use.

By the mid-1960s, GeO_2 was being used in Japan as a polymerization catalyst for PET made for use as transparent bottles and as nonyellowing textile fiber. American manufacturers preferred to use the cheaper antimony trioxide (Sb_2O_3) catalyst for most PET products. By the mid-1990s, however, catalytic use of GeO_2 in the United States had grown, and statistics on its use started to be published in the U.S. Geological Survey (USGS) Minerals Yearbook U.S. Geological Survey, 1997-2000). In 2000, it accounted for about one-fourth of the domestic germanium market.

The end uses of germanium are examined in more detail in the “Uses” section, but the following timeline that lists selected milestones provides some historical perspective (table 1).

Table 1. Timeline for selected germanium uses

WW II	Germanium diodes developed for use in radar systems.
1948	Diodes; triode (transistor) developed; optical glasses; phosphors.
1949	Infrared lenses.
1951	Junction transistor developed.
1953	Tetrode and pentode transistors developed.
1954	Large industrial germanium rectifiers are in use.
1957	Germanium transistor formed as part of a printed circuit.
1960	Germanium tunnel diode developed.
1965	Polymerization catalysts used extensively in Japan; use of germanium as a gallium-doped single crystal in radiation detectors.
1972	Germanium-platinum petroleum reforming catalyst patented.
1975	Use of germanium in light-emitting diodes (LEDs).
1978	Liquid-crystal displays (LCDs) are supplanting LEDs; germanium use in fiber optics is being developed.
1983	Fiber optics—substitution of monomodal for multimodal fibers.
1997	Germanium polymerization catalysts in significant use in the United States.

Description

Salient Facts

Germanium is a grayish white metalloid or semimetal, a semiconductor that has electrical properties between those of a metal and an insulator. In the second half of the 20th century, germanium became the essential element in many new solid-state electronic and optical devices. In the periodic table, it is element number 32, has atomic weight 72.59 and electron configuration $[\text{Ar}]3d^{10}4s^24p^2$, and is located in period 4, group 14 (IVA in the old notation). Germanium is nominally tetravalent but possesses seven oxidation states, of which +4 and +2 are the most stable, with -4, 0, +1, +3, and +5 being much less stable. Natural germanium is a mixture of five stable isotopes—by weight, Ge^{74} (35.94 percent), Ge^{72} (27.66 percent), Ge^{70} (21.23 percent), Ge^{73} (7.73 percent), and Ge^{76} (7.44 percent). In addition, 33 radioactive isotopes have been identified, of which two have half-lives measured in days, and the rest have half-lives that range from 20 milliseconds to 39 hours.

Like two other elements in group 14, carbon and silicon, germanium crystallizes in the covalently bonded cubic diamond structure, from which it melts at 937.4°C . Its room temperature density, 5.32 grams per cubic centimeter, is slightly less dense than that of the molten liquid. Although germanium has the appearance and luster of a metal, it is brittle and hard, with a Mohs hardness of 6—a little softer than silicon and very much softer than the diamond form of carbon.

Chemically, germanium is stable in air up to 400°C , above which it begins to oxidize. It is not attacked appreciably by mineral acids, such as hydrochloric acid (HCl) or hydrofluoric acid (HF), unless an oxidizer is present and is attacked only slowly by hot concentrated sulfuric acid. It is, however, somewhat more readily attacked stepwise by nitric acid and by aqua regia. In these acids, it is first oxidized, and the oxide then is dissolved. Germanium is not attacked appreciably by aqueous caustic solutions; however, it does dissolve readily in molten sodium or potassium hydroxides to form germanates and in molten nitrates and carbonates (Plunkert, 1985; Adams and Thomas, 1994, p. 542).

Optically, germanium is transparent to near-IR radiation in the wavelength range of 1,800 to 23,000 nanometers (nm). It has a high refractive index for IR (4.0026 at 11,000 nm) together with low chromatic dispersion (the variation of refractive index with wavelength). Its oxide glass also has a high refractive index and low dispersion.

Electrically, germanium is an intrinsic n-type (electron) semiconductor and, compared with metals, is a poor conductor, having a resistivity of 53 ohm-centimeters (ohm-cm) at 25°C , compared with 1.7×10^{-6} ohm-cm for copper.

Principal Forms, Alloys, and Compounds

Metal and Alloys

Germanium as reduced from GeO_2 is a metal powder, which is then melted and cast into what are called first-reduction or as-reduced bars. These bars are then zone-refined to a highly pure polycrystalline metal that is either used directly in that form or converted to single-crystal form. Most germanium passes through one or both of these purified metal forms before being used directly or being converted into highly pure compounds (Adams and Thomas, 1994, p. 547).

Germanium forms alloys with many metals. Harner (1961) described a partial list of 21 such metals, including all the base metals and most precious metals. About one-half of these germanium-metal systems contain intermetallic compounds. Alloys, however, are minor uses for germanium. Their utility is described in the “Uses” section.

Compounds

From the large number of known germanium compounds, a few classes can be identified as the principal compounds of commercial importance. First, among the halides, germanium tetrachloride (GeCl_4), which is derived from the treatment of zinc smelter residues, is the feedstock from which germanium metal and germanium compounds are made. Germanium tetrabromide (GeBr_4) and germanium tetraiodide (GeI_4) are easily prepared, and germanium tetrafluoride (GeF_4) is prepared with somewhat less ease.

Both germanium monoxide (GeO) and germanium dioxide (GeO_2) are manufactured, but the latter is the commercially important compound. As prepared by the hydrolysis of GeCl_4 , GeO_2 is in the “soluble” hexagonal form, in which it is, to some extent, soluble in water, hydrochloric and hydrofluoric acids, and alkali hydroxide solutions. This form can be converted by heating to the “insoluble” tetragonal form, which is nearly one-half again as dense and is insoluble in aqueous solutions of acids or alkali hydroxides. A noncrystalline (glassy) dioxide can be made by melting either of the solid forms and quenching from the melt.

Among the germanates, which are made by fusing GeO_2 with alkali oxides or carbonates, the most important are the scintillation phosphor ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) and the fluorescent lamp phosphor ($\text{Mg}_6\text{Ge}_3\text{O}_{12}$).

At least 200 germanides, which are prepared by melting or sintering germanium with other metals, are known. Finally, several organometallic compounds of germanium are of some interest in medicine in the treatment or prevention of cancer and high blood pressure (Adams and Thomas, 1994, p. 543-544).

Commercial Grades, Shapes, and Specifications

Zone-refined crystalline germanium typically is 99.9999 percent pure germanium. Total impurities are typically less than 100 parts per billion (ppb), and electrically active impurities, less than 0.5 ppb. For extremely demanding uses, germanium is zone-refined to contain less than 0.0003 ppb total impurities. Germanium also is available as germanium tetrachloride, high-purity oxides, first-reduction ingots, single-crystal bars and castings, doped semiconductor wafers, optical blanks, and other specialty products. Polycrystalline metal is made in castings up to 115 kilograms (kg), and single crystals are grown as large as 90 kg (Adams and Thomas, 1994, p. 547).

Specifications for permissible impurity contents of the different grades of germanium metal as well as for such properties as volatile content, bulk density, and electrical resistivity are covered in several American Society for Testing and Materials (ASTM) standards.

Sources of Germanium

Primary Germanium

The mean germanium content of the Earth's crust is in the range of 1.0 to 1.7 parts per million (ppm) and is usually placed at 1.4 or 1.5 ppm. Thus, germanium is a little more abundant than molybdenum or tungsten and somewhat less abundant than beryllium or tin. Its mean concentration in the major classes of rocks lies in the following ranges: igneous rocks, 1.0 to 1.6 ppm; sedimentary rocks, excluding coal, 0.4 to 2.2 ppm; and coal, 5.5 ppm. In ground water, the mean is about 300 parts per trillion (ppt); in river water, 50 ppt; and in seawater, it is 60 ppt (Weeks, 1973; Bernstein, 1985, p. 2410).

Germanium is a dispersed element. In nature, it never exists as the native metal and is only rarely found in commercial quantities in the few minerals in which it is an essential component. Rather, it occurs in trace amounts in many minerals, including some of the common metallic ore minerals. In these, it substitutes in the crystal lattice for arsenic, gallium, silicon, tin, zinc, and other elements. In coal, germanium is associated with the organic content

rather than with the mineral content of the beds. It is most highly concentrated in the glassy translucent component of coal known as vitrain (Stadnichenko and others, 1953, p. 1). Germanium is widely dispersed in silicate minerals but is found in higher concentrations in some sulfides and oxides. Bernstein (1985, p. 2411) listed 16 minerals in which germanium is an essential constituent. Of these, about one-half are known principally or solely from two copper deposits in Africa—Tsumeb in Namibia and Kipushi in Zaire. Two of the minerals, germanite and renierite, have been recovered as distinct, if still subsidiary, ores of germanium at the African deposits. The germanium content of eight of these minerals is listed in table 2.

Table 2. Selected germanium minerals
[Modified from Weeks (1973)]

Mineral	Composition	Germanium content (weight percent)
Renierite ¹	(Cu,Fe,Ge,As,Zn)S	4.6-9.2
Germanite ²	Cu ₁₁ Ge(Cu,Ge,Fe,Zn,W,Mo,As,V) ₄₋₆ S ₁₆	6.2-10.9
Argyrodite	Ag ₈ GeS ₆	6.4
Fleischerite	Pb ₃ Ge(SO ₄) ₂ (OH) ₆ •3H ₂ O	7
Itoite	Pb ₃ Ge(SO ₄) ₂ O ₂ (OH) ₂	7.6
Schaurteite	Ca ₃ Ge(SO ₄) ₂ (OH) ₆ •3H ₂ O	13.4
Briartite	Cu ₂ (Fe,Zn)GeS ₄	18.5-18.9
Stottite	FeGe(OH) ₆	31.5

¹Bernstein, 1986b, p. 213

²Palache, Berman, and Frondel, 1944, p. 386; Bernstein, 1986a, p. 1686.

Weeks (1973) listed 15 ore minerals in which germanium is locally present. Germanium is most often found in the zinc sulfide minerals sphalerite and wurtzite (both ZnS) and, less commonly, in the copper minerals chalcopyrite (CuFeS₂), enargite (Cu₃AsS₄), bornite (Cu₅FeS₄), and tennantite (Cu₁₂As₄S₁₃). Most of the world's supply of germanium is a byproduct of zinc smelting, with an additional smaller amount derived from copper smelting; both sources reflect an origin in sulfide ores. Some germanium was also extracted from fly ash at coal-burning powerplants in China, the United Kingdom, the Commonwealth of Independent States, and perhaps elsewhere as well.

Ore deposits in which germanium is found are characterized by abundant base metals, especially zinc and copper. The most commercially important germanium-bearing ore deposits are low-temperature zinc or lead-zinc deposits, such as those in the tri-State district of Kansas, Missouri, and Oklahoma and in the upper Mississippi Valley region. "The geologic environment most favorable for large zinc sulfide deposits [including those bearing germanium] is in sedimentary sequences which include carbonate rock strata that have been permeated by mineralizing solutions" (Weeks, 1973). Some complex copper-arsenic-antimony-tin deposits, such as those at Butte, Mont., Chuquibambilla, Chile, and other localities, also contain significant germanium, although it is not always recovered.

U.S. reserves of germanium are located mainly in the zinc deposits of the Red Dog district of Alaska, with lesser amounts in the zinc ores of central Tennessee. The quantities are considered to be company confidential data and are not available for publication. Comparable figures for other countries are also unavailable. (The definitions of reserves and reserve base can be found in the "Appendix.")

Secondary Germanium

Because of the small quantities in which germanium is used in most manufactured products, little if any germanium is recovered from old (postconsumer) scrap. However, more than one-half of the germanium used in manufacturing electronic and optical devices is returned as new (manufacturing) scrap for recycling. One domestic company reported the recovery and reuse of 70 to 80 percent of the germanium consumed in its production of optical fibers (Lucent Technologies Inc., 1997). Worldwide, between 25 and 35 percent of the total germanium used is

derived from recycled scrap.

Production Technologies

Broadly speaking, the extraction of germanium from its ores can be divided into two stages—the production of a germanium concentrate, usually germanium sulfide or oxide, followed by its chlorination and subsequent purification. When the feed material is scrap germanium, it is converted to GeO_2 where necessary and then processed in the same way as ore concentrates.

To prepare germanium concentrates, copper-lead concentrates of the sort formerly produced at Tsumeb, Namibia, are retorted, with sublimation and collection of germanium sulfide (GeS_2). Copper-zinc concentrates in Zaire have been roasted with sulfuric acid, followed by selective precipitation of GeO_2 with magnesium oxide. Where the germanium is contained in zinc concentrates and the concentrates are processed pyrometallurgically, they are first roasted and sintered. The sinter fume is collected, leached with sulfuric acid, and GeS_2 is precipitated from the solution with hydrogen sulfide or tannic acid. At electrolytic zinc plants, which have largely supplanted pyrometallurgical plants, the zinc sulfate solution must be purified before electrolysis. Germanium, iron, and other impurities are precipitated from the solution during purification.

Where some of the above processes yield GeS_2 rather than GeO_2 , the product is treated with an oxidizer, such as sodium chlorate, to convert the GeS_2 to the GeO_2 , which is dissolved in concentrated HCl, producing germanium tetrachloride (GeCl_4) (Adams, 1990). The GeCl_4 is purified in the germanium refinery by fractional distillation in glass or fused quartz equipment; the procedure is modified as needed with steps to remove specific objectionable impurities. Subsequent processing is as shown in the simplified flow diagram in figure 1.

The purified GeCl_4 is hydrolyzed with deionized water to yield GeO_2 . After drying, the GeO_2 is reduced with hydrogen at 760°C to form germanium metal powder, which is then melted and cast into bars, known as first-reduction or as-reduced bars. The bars are then zone-refined to polycrystalline metal that typically contains less than 100 ppb total impurities and less than 0.5 ppb electrically active impurities.

The purified metal either is used in the polycrystalline form or, for electronic and some optical uses, is converted to single crystal ingots by the Czochralski method. The growth of single crystals is a batch process, in which the electronic properties prescribed for the batch are obtained by adding dopants to the melt from which the crystal is grown very slowly, under closely controlled conditions. The single crystal is sliced into wafers for electronic use or shaped otherwise for optical use. Polycrystalline ingot may be remelted and cast into lens blanks (Adams and Thomas, 1994, p. 545-547).

Uses

Germanium owes its usefulness to at least five salient properties. First, it is an intrinsic semiconductor, which in the pure state—in the absence of contaminant elements in its crystal structure—will conduct electricity, albeit poorly. It is particularly effective at high frequencies and low operating voltages. Second, germanium is transparent to part of the infrared spectrum, whether in the crystalline or glassy states. Third, like silicon, it is a glass-former, able to form extended three-dimensional networks of more or less randomly ordered germanium-oxygen tetrahedra. Fourth, it has an exceptionally high refractive index. Fifth, it exhibits low chromatic dispersion. These five properties, singly and sometimes in combination, determine the usefulness of germanium in electronics devices, solar power arrays, night vision devices, optical lens systems, and fiber optics. A sixth property, specific to a single but commercially important use, is the ability of germanium to catalyze the polymerization of the commodity plastic PET without undesirable coloring of the plastic product.

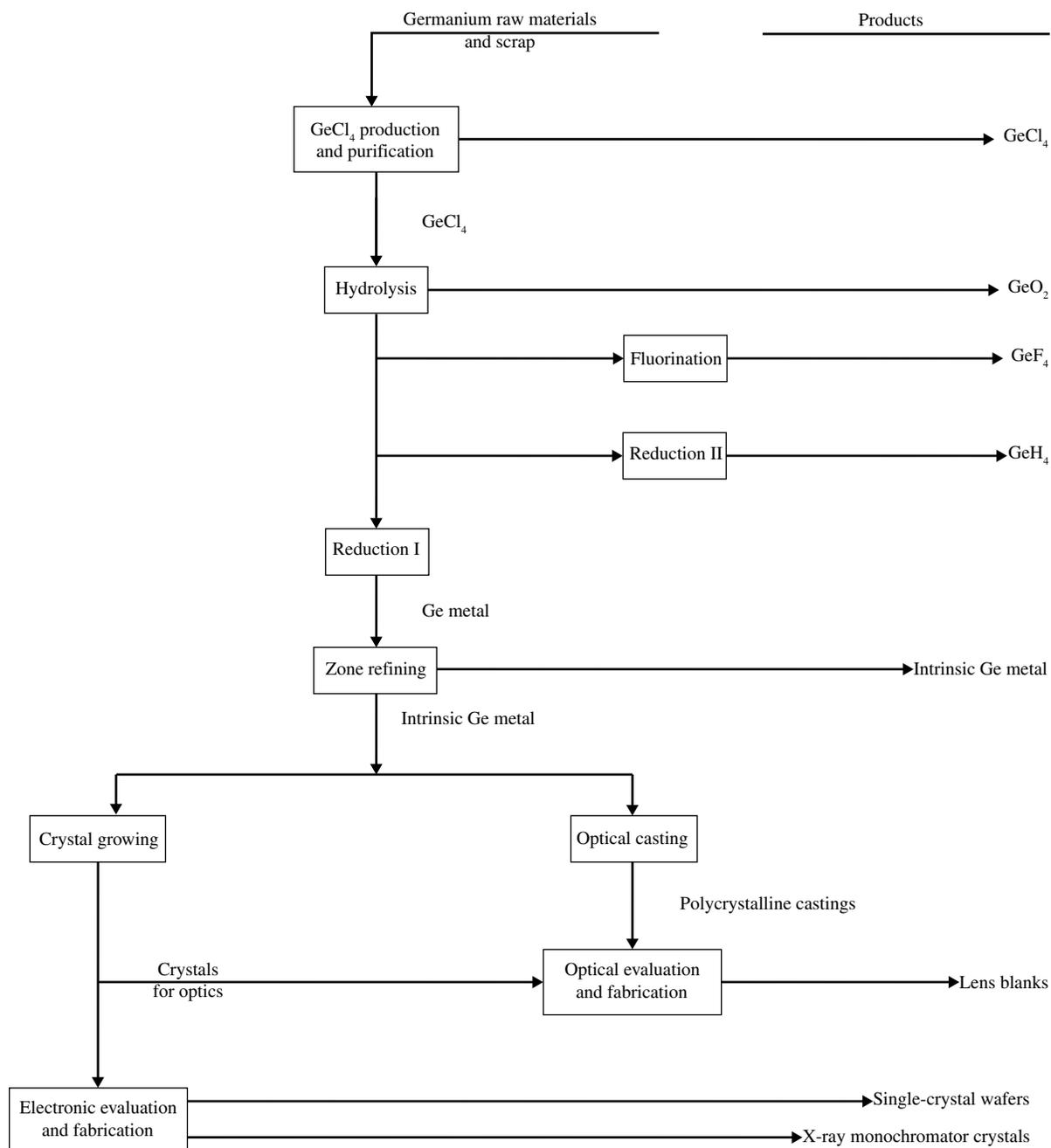


Figure 1. Germanium processing simplified flow diagram. Reproduced from Adams and Thomas, 1994, p. 546, with permission.

Principal Uses

A consistent set of germanium end-use consumption data for the United States is available in the BOM and USGS Minerals Yearbooks since 1980 (U.S. Bureau of Mines, 1937-1995; U.S. Geological Survey, 1997-2000). A new category, “electrical/solar panels” was established in the 1996 yearbook; it has been renamed “electronic and electrical uses” for this report. Consumption of germanium for radiation detectors was moved into the new category

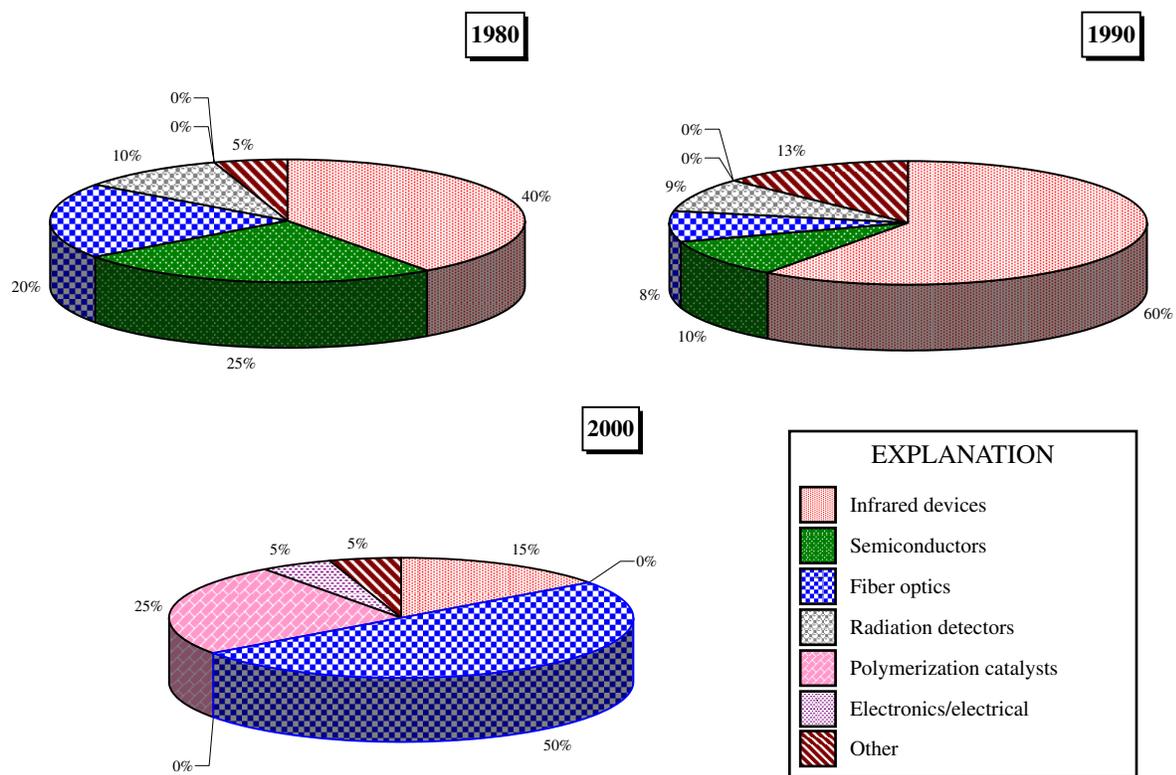


Figure 2. Shifts in the pattern of U.S. germanium use. Data from U.S. Bureau of Mines, 1980, 1990; U.S. Geological Survey, 2000.

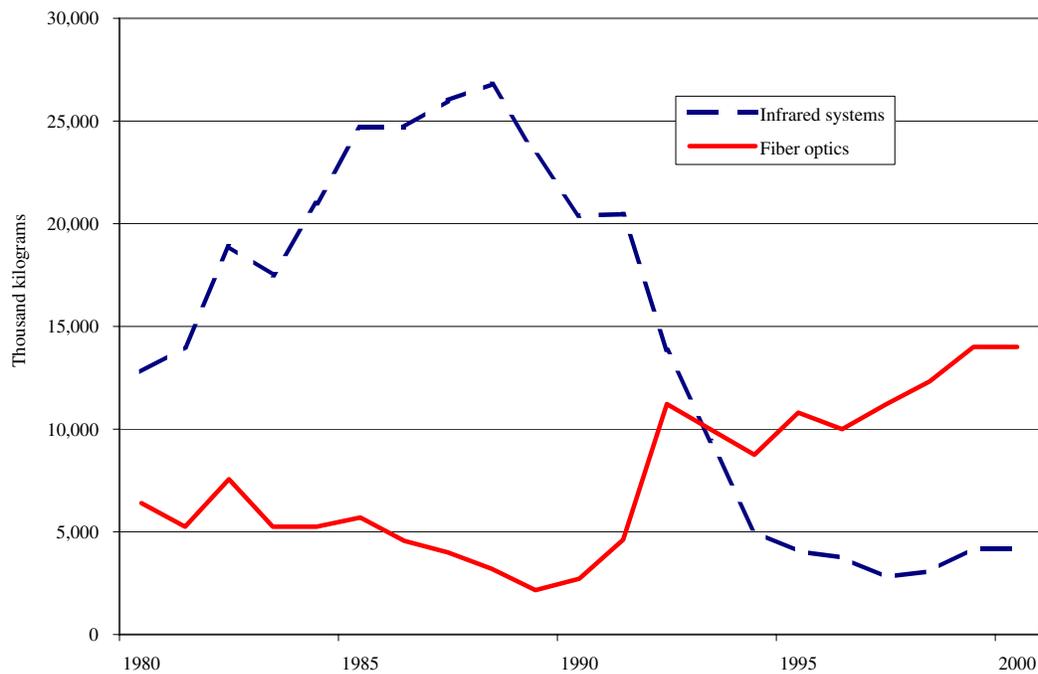


Figure 3. U.S. consumption of germanium for the two principal uses. Data from U.S. Bureau of Mines, 1980-1994; U.S. Geological Survey, 1995-2000.

beginning in 1996, and consumption for semiconductors, beginning in 1997. Shifts in the consumption pattern during the past two decades are indicated in figure 2. Trends in two of the principal uses, IR systems and fiber optics, can be followed throughout the period as shown in figure 3.

Fiber Optics

Fiber optics has been an important use for germanium for at least two decades. Consumption for fiber optics grew rapidly in the 1990s and, before the end of the decade, accounted for one-half of the germanium used in the United States annually (figs. 2, 3). The trunk lines of telephone systems (the long-distance land and submarine lines) were, until the 1980s, copper lines. By the end of the century, these had nearly all been replaced, in the United States and many other industrial countries, with fiber optic lines of vastly greater information-carrying capacity. The fibers used in long-distance cables are silica fibers 7 to 10 micrometers (μm) in diameter (about one-tenth the thickness of human hair), which are doped with GeO_2 . Worldwide, some 600 million kilometers of optical fiber is now deployed; thus, the consumption of germanium in this use is large enough to be measured in tons (Dennis W. Thomas, Eagle-Picher LLC, written commun., April 29, 2003).

Several transparent materials—chalcogenide, fluoride, germanate, and silica glasses, as well as plastics—have been employed as optical fibers for the transmission of analog or digital information. But by far the most important commercial fibers have been essentially silica glass doped with at most 4 weight percent GeO_2 , which is useful as a glass component because of its transparency to near-IR radiation (the part of the spectrum used in all commercial fiber-optic data transmission), its high refractive index, and its low chromatic dispersion.

Germanium is used in two distinct kinds of optical fiber. The single-mode stepped-index fiber is the very thin fiber used in long-distance cables. It transmits digital information accurately at very high rates (100 gigabits per second) with low signal attenuation. Signal strength is maintained by repeaters (amplifiers) located every 50 to 100 kilometers along its length. This kind of fiber is used for transmission in the 1,300-nanometer (nm) or 1,550-nm IR telecommunications windows. The “light” signal is a relatively powerful intensity-modulated monochromatic radiation generated by a laser. Splicing or connecting a cable containing such fibers is an exacting and expensive operation.

The second kind of optical fiber is the multimode fiber, used for transmission over much shorter distances, such as between telephone central offices and the concentrators that serve a few hundred homes or between and within office buildings or to connect the equipment within local-area computer networks. Multimode fibers range from 50 to 85 μm in diameter for the graded-index type and 50 to 300 μm for stepped-index types. Both types of multimode fiber are used for transmission of either analog or digital signals in the 800-nm or 1,300-nm wavelength windows, typically using radiation produced by LEDs but sometimes by lasers. The LED radiation is less powerful and less monochromatic than laser radiation, but LEDs are much less expensive than lasers. Fiber bandwidth, which is inversely proportional to length of fiber, is limited to about 20 megahertz-kilometers (MHz·km) in the step-index type but can be as high as 1,000 MHz·km in the graded-index type. Connection of these larger fibers is done much more readily and economically than with the small single-mode fibers (Crisp, 2001, p. 22-38; Hecht, 2002, p. 67-96).

Consumption of germanium for fiber optics in the United States has averaged about 12 metric tons per year (t/yr) since 1995. Whatever the present disposition of germanium among the various types of optical cable, it would seem that the short-distance multimode fibers will require more germanium than the long-distance single-mode fibers in the next few years. This conjecture is based on the larger physical bulk of the multimode fibers, the generally higher percentage of germanium in their glass, and the perception by telecommunication industry analysts that the long-distance single-mode-fiber infrastructure has been overbuilt and that it may be several years before significant new capacity is required.

Catalysts

GeO_2 is used as a polycondensation catalyst for the late-stage polymerization of PET, which is a large-volume commodity plastic used in bottles, films, food packaging, and many other products. GeO_2 yields a product with better transparency and whiteness than do other catalysts and has been used for decades in Japan. In the United

States, it was considered too expensive for many uses of PET, and Sb_2O_3 or antimony triacetate [$\text{Sb}(\text{CH}_2\text{COO})_3$] were used instead. The use of GeO_2 as a catalyst was not reported separately in USGS statistics until 1997; quantities used prior to that year were included in an “other uses” category. Before the mid-1990s, the quantity is believed to have been small, perhaps less than 2 t/yr, but by 2000, it had grown to 7 t/yr, or one-fourth of total domestic germanium consumption.

Germanium compounds are currently being investigated as catalysts for the fluorination of a variety of hydrocarbons. Of particular interest is the manufacture of hydrofluorocarbons (HFCs), the environmentally friendly refrigerants that are the successors to chlorofluorocarbon (CFC) refrigerants. The germanium-catalyzed synthesis, which takes place at a lower temperature and pressure than current processes, promises to be energy efficient and highly selective, minimizing the synthesis of unwanted byproducts (U.S. Department of Energy, 2001).

Infrared Optical Systems

The ability of germanium oxide glasses and germanium metal to transmit near-IR radiation in the 1,600- to 18,000-nm range has long been applied in night vision systems of the passive kind. Germanium is readily machinable into IR windows and lenses, and its high refractive index and low chromatic dispersion allow the use of simple, sometimes uncorrected, lenses in IR imaging systems. In addition, germanium is mechanically strong, hard, and has good thermal conductivity—valuable properties for imaging devices, most of which are employed for military or security surveillance purposes and subject to rough use in harsh, wide-ranging environments.

The passive devices, or thermal imagers, mentioned above are sometimes referred to as forward looking infrared (FLIR) devices and are distinct from active systems, which emit radiation and measure the radiation reflected differentially from objects in the field of view. FLIR devices form images by sensing the thermal contrast between objects and background. They can work in complete darkness and are not affected by smoke or fog. They have supplanted active devices in military use because, among other reasons, the radiation emitted from an active device makes it locatable. Military germanium-based FLIR systems are used in night vision goggles, binoculars, gunsights, surveillance cameras, and IR- (heat-) seeking missiles. Civilian uses include some of those same uses, and others, such as detecting overheating bearings, fire fighting in dense smoke, locating lost hikers in wilderness areas, monitoring of rock surface temperatures in mines, satellite mapping, medical diagnosing, and detecting faults in structural materials (Roskill Information Services Ltd., 1990, p. 112-117). Germanium also is used for lenses for IR lasers, especially the industrially important carbon dioxide lasers used for cutting, drilling, and welding metals.

Electronic and Electrical Uses

The ways in which germanium is used in electronics devices stem from its properties as a semiconductor. Germanium was the first commercially important semiconductor. Although electronics was the principal use of germanium through the 1950s, 1960s, and most of the 1970s, it had diminished by 2000 to only 5 percent of total germanium use in the United States. Most transistors and diodes used at the beginning of the 21st century are silicon-based; they are preferred to germanium devices because of ease of manufacture, better temperature stability, and higher maximum operating temperature (150°C versus 100°C). Although they are less efficient than silicon diodes, germanium diodes are preferred in some circuits because they start conducting at lower voltage [0.2 to 0.3 volts (V) versus 0.6 V].

Interest in germanium as an electronics material has been revived in the past 2 or 3 years by the development of a successful method for growing exceedingly thin epitaxial layers of germanium on silicon. Microscopic bipolar on-off transistors that incorporate silicon germanium, as it is known, are currently being designed into the chips used in cell phones, computers, and lasers. These transistors are five times faster than comparable silicon transistors and twice as fast as high-speed indium phosphate transistors. In addition, they use much less power than standard transistors. Chips that incorporate silicon germanium are expected to be ideally suited to the broadband requirements of hand-held personal communications devices and the electronics signal processors linked to fiber optic cables (Patch, 2001; IBM Microelectronics, undated).

Single-crystal germanium is used as a substrate for epitaxial deposits of gallium arsenide (GaAs) and gallium arsenide phosphide, which are used in LEDs, laser diodes, and photovoltaic solar cells. Use in LEDs has moderated because LEDs have been replaced in many applications by LCDs. The potential for use in multilayer solar cells appears to be good, as triple-junction gallium indium phosphide on GaAs on germanium solar cells have been constructed for use in concentrator-type solar panels for terrestrial as well as space use. The new cells convert 32 percent of the incident energy to electric power. These multilayer cells convert a larger segment of the spectrum to electrical energy than do cells currently in production. The top layer converts the highest energy light, and the middle and bottom layers each convert part of the light spectrum that reaches them; thus each layer contributes to the cell's conversion efficiency. A four-junction solar cell being studied in the late 1990s could possibly realize a conversion efficiency as high as 40 percent (Environmental News Network, 1999).

A new germanium-based photodetector was in production in 2002. It is designed for feedback control of the output power of lasers used in fiber optic telecommunications systems. Such lasers must be operated at a constant power level to maintain signal quality (Spectrolab Inc., 2002).

Although germanium has largely faded from large-scale use in electronics, it is still used in important quantities in power rectifiers that are employed in electric motor controllers, backup power supplies for emergency lighting and computers, and low-voltage power supplies for various electrical devices.

Other Uses

Although relatively little germanium is used in alloy form, there are a few alloys that have proven useful. An 88-percent-gold–12-percent-germanium alloy, with a melting temperature of 359° C, has been used as a solder for gold jewelry (Brady and Clauser, 1997). Germanium also is alloyed in several combinations with gold, silver, copper, and palladium in dental alloys and with silicon in thermoelectric devices. More often, germanium is used in very small quantities as a hardener of metals, such as aluminum, magnesium, and tin.

Because of its high refractive index and low chromatic dispersion, GeO₂ has long been an ingredient of the glass used in wide-angle camera lens. Single-crystal germanium is used in detectors for gamma rays in spectral analysis and in x-ray monochromators for high-energy physics. Niobium germanide is a superconducting compound. Germanium resistance thermometers are used for precision temperature measurement for the range from 0.5 to 100 K (Scientific Instruments, Inc., undated). In medicine, scintillation crystals of bismuth germanium oxide are used in positron emission tomography scanners (Adams and Thomas, 1994, p. 551-552).

Trends in Use

Consumption of germanium in fiber optics first appeared as a separate end-use category in data published by the BOM in 1980, when it accounted for 20 percent of domestic germanium consumption (U.S. Bureau of Mines, 1937-1995). In the 1980s, the telecommunications industry emphasized the building of long-distance fiber optic networks. The small monomode fibers used for those networks did not contain much germanium; thus, consumption for fiber optics declined during the decade. After 1990, however, consumption picked up very rapidly, reaching 34 percent of domestic germanium consumption in 1992, 40 percent in 1995, and 50 percent in 1999, as shown in figure 3.

In a field closely related to fiber optics, germanium sulfide glasses are being investigated as possible replacements for single crystals of germanium that are used in a wide range of nonlinear photonic devices (Institute for Materials Research, University of Leeds, 1999).

Apparently, the market for PET products has shifted in recent years to include products for which good appearance is important, such as beverage bottles. For these products, GeO₂ is used as the polycondensation catalyst, in preference to antimony oxide. Germanium catalyst use rose rapidly in the mid-1990s, but the data reported since then cover only 4 years, and a definite trend is not yet apparent.

Military demand for devices for aerial surveillance, fusing, and night vision has dominated the market for IR systems for many years. Through most of the 1980s, military demand fueled growth in germanium consumption,

but beginning in 1989, consumption began to fall sharply, finally leveling out at 3 to 4 t/yr in the late 1990s. The civilian market for night surveillance cameras and other devices appears to have compensated for some of the reduction in demand for military applications.

The trend in consumption of germanium for electronic and electrical uses has been downward for the past three decades. Although germanium is still of technical importance in these uses, they are likely to continue to account for only a small segment of the germanium market unless multijunction solar cells become a commercial success, in which case the demand for germanium could increase significantly.

Substitutes for Germanium

Although germanium-doped silica fibers are the standard optical fibers in use, other types of optical fibers have potential to displace them, at least in some kinds of networks. Two families of glass suited for IR transmission are similar in general to conventional germanium-silica fibers. These are the germanium-oxide-based glasses and fluoride glasses. The oxide fibers, made of GeO_2 (30 to 76 percent), alkaline earth oxide (15 to 43 percent), and aluminum, gallium, or indium oxide (3 to 20 percent), have unusually high thresholds for laser damage at 3,000 nm and transmission losses of less than 1 decibel per meter over the range from 1,000 to 3,000 nm. The best known fluoride glasses are the fluoroaluminate and fluorozirconate types. These glasses have very low transmission losses, about one-tenth that of silicate optical fiber glasses, and transmit over a much wider span of the electromagnetic spectrum. The theoretical losses are especially low for the fluorozirconate glass called ZBLAN [zirconium (Zr), barium (Ba), lanthanum (La), aluminum (Al), sodium (Na) fluoride], which has the potential to carry 100 times as much information as silica fiber. When fabricated into fibers, however, partial crystallization of this glass nullifies its potential advantage, and the best ZBLAN fibers being made in the late 1990s could carry only about one-fifth the information carried by silica fibers (National Aeronautics and Space Administration, Marshall Space Flight Center, 1997; Rutgers University, undated).

Air-cored glass or polymer fibers are said to hold great promise for certain kinds of telecommunication applications. In these fibers, light is confined to the hollow center of the fiber by total internal reflection from the surrounding glass or polymer, which is honeycombed with an ordered array of longitudinal holes (Optics.org, 2001).

Sb_2O_3 and $\text{Sb}(\text{CH}_2\text{COO})_3$ are acceptable polymerization catalysts for many uses of PET where appearance is not of paramount importance. Titanium alkoxides also are effective catalysts but cause yellowing of the polymer, which excludes them for several end uses of PET. Growth in the demand for GeO_2 catalysts for PET could be slowed by competition from the new polymer polyethylene naphthalate (PEN), which is replacing PET in some photographic films, magnetic recording tape, film for flexible printed circuitry, and other high-performance applications. Nongermanium compounds appear to be favored for the catalysis of PEN films. Competition from new nongermanium catalysts also could slow the growth of germanium PET catalysts (Teijin Limited, 2001; Toyobo Research Center Ltd., undated).

Other semiconductors are transparent to IR radiation, but germanium is the most satisfactory for the near-IR range, in which it is used. It can be replaced, with less satisfactory overall performance, by zinc selenide or ZnS (Roskill Information Services Ltd., 1990, p. 114).

Several semiconductors, chiefly silicon, and also semiconducting compounds, such as GaAs and indium antimonide, compete with germanium and can replace it in most semiconductor applications. Whether they actually displace germanium from any given circuit component depends on the effects of substitution on the functioning of the component, on ease of manufacturing, and on cost.

Industry and Market

Germanium-bearing zinc ores are mined in the United States at Cominco Ltd.'s Red Dog Mine in northern Alaska and Savage Resources Ltd.'s Elmwood-Gordonsville Mine in Tennessee. Zinc concentrates produced in Alaska are exported to Cominco's smelter in British Columbia, Canada, and to several other countries. Germanium

smelter residues from Tennessee are exported to Umicore, SA (formerly Union Minière SA's Electro-Optic Materials Business Unit) in Belgium for recovery and refining of the germanium. Both mining companies supply domestic as well as foreign processors of germanium-bearing products.

Germanium and its compounds are produced at three domestic refineries from domestic and imported concentrates (zinc smelter residues), semirefined materials, and scrap. The Electro-Optic Materials Department of Eagle-Picher Industries Inc. in Oklahoma and North Carolina is the largest domestic producer. Indium Corporation of America in New York produces germanium from imported scrap and semirefined materials.

Worldwide, germanium products are processed by 17 companies in 12 countries. Sixteen of the companies produce germanium metal, but only seven produce GeO_2 (Moreno, 2000, p. 707-708). Unwrought or semiwrought forms of germanium are traded by 93 companies in 31 countries; the dioxide is traded by 68 companies in 27 countries (Moreno, 1997, p. 502-504). The number of companies that manufacture germanium-containing products has not, as far as is known, been compiled, but one may surmise from the highly technical nature of its uses that the number does not exceed a few dozen.

The value of domestic refinery production of zone-refined germanium in 2000 was estimated by the USGS to be about \$29 million, based on the average producer price of \$1,250 per kilogram for that year (Brown, 2002). On that same basis, world refinery production was probably worth about \$120 million. As a high-unit-value commodity, germanium is traded internationally in its several forms unconstrained by transportation costs. The flow of germanium concentrates and processed forms tends to be from the larger producers, such as Belgium and China, towards the principal users—Japan, the United States, and Western European countries. Prices for germanium metal and GeO_2 are published monthly and weekly in trade journals, such as *Metal Bulletin*, *Platts Metals Week*, and *Mining Journal*.

Germanium and the Environment

Germanium is a relatively nontoxic element that poses no appreciable threat to the environment. In nature, it typically is dispersed in trace amounts in other minerals, and the quantities recovered and used are small compared with those of other materials. In its recovery from ores and processing, germanium is associated with arsenic and cadmium, against which precautions must be taken; however, these elements can be controlled in the work environment and prevented from endangering the natural environment. In manufacturing, inhalation of germanium dust from grinding or polishing is not known to cause health problems. However, the amount of germanium set free from the combustion of coal at industrial plants is considerable. It has been estimated that 2,000 t/yr goes into ashes, flue dust, and stack gases in the United Kingdom; it is not stated how much of that quantity escapes to the atmosphere and how much is trapped at the plants (Spectrum Laboratories Inc., 2001).

Germanium compounds also are relatively benign, with the notable exception of germanium hydride (GeH_4), which is toxic, and germanium tetrafluoride (GeF_4), which hydrolyzes in moist air, forming highly corrosive HF. "The dioxide has low toxicity and limited bioavailability in the environment. It poses no immediate ecological risk" (Cominco Ltd., 2000).

No governmental air quality standards or workplace exposure limits have been formulated for germanium in the United States.

Supply, Demand, and Sustainability

The United States accounts for about one-fourth of world production of refined germanium. In 2000, this amounted to 23 metric tons (t) of primary and secondary germanium compared with the estimated world total of 71 t of primary germanium, as shown in figure 4. World secondary production (including that embedded in the U.S. refined production figure) was estimated to be about 25 t. Other significant producers include Belgium, Canada,

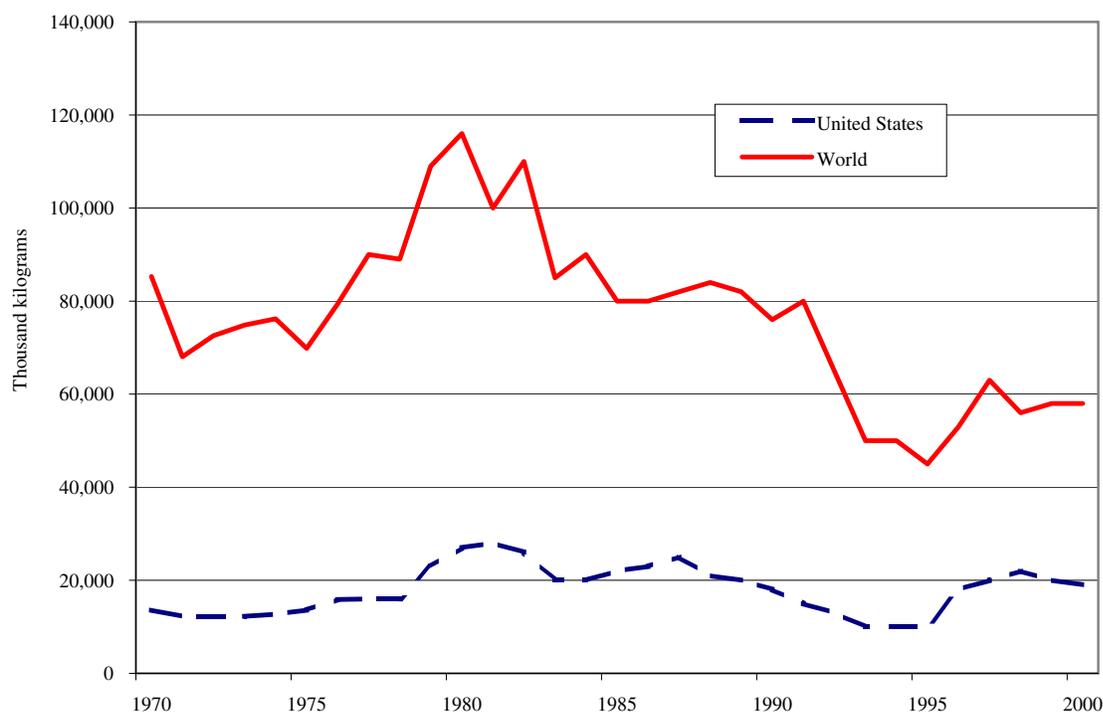


Figure 4. Production of refined germanium. Data from U.S. Bureau of Mines, 1970-1994; U.S. Geological Survey, 1995-2000.

China, Germany, Japan, Russia, and Ukraine.

U.S. imports of germanium are substantial; most come from Belgium, China, and Russia. However, figures on imports of GeO_2 and other compounds are not available, and imports of germanium metal and waste and scrap are grouped into one category and reported in units of gross weight. For the years listed in table 3, the import figures for unwrought, waste, and scrap germanium have been adjusted to yield, very approximately, the germanium content. In 2000, these partial imports, together with sales from the National Defense Stockpile (NDS), satisfied more than one-third of U.S. consumption; domestic refined production accounted for the other two-thirds (table 3, fig. 5). Sales of germanium from the NDS have been a significant part of the domestic supply since 1997.

Total estimated domestic germanium consumption has, since the early 1960s, ranged between 20 and 40 t/yr. Since 1992, the range has narrowed to 25 to 30 t/yr, and since 1997, the estimate has been unchanged at 28 t/yr. World consumption since the mid-1990s has been estimated to be in the range of 80 to 100 t/yr (Roskill's Letter from Japan, 1999, 2001).

Data for U.S. and world germanium resources are not available for publication. If depleted at the 2001 rate, domestic resources would probably last several decades. It is likely that any domestic shortage of germanium could be postponed by extracting the element from coal ash and flue dust and from some copper ores from which it is not currently being recovered.

Barring a large increase in demand, the production, use, and recycling/disposition of germanium appear to be sustainable. No deleterious health or environmental effects are likely to be associated with its production or use, and because reserves normally are replaced partially or completely as they are used, they are likely to last considerably longer than 2000 estimates might suggest.

Table 3. U.S. supply and demand for unfabricated germanium.

[In kilograms of contained germanium. °estimated. NA not available. — zero. Data include estimates. All data are rounded to three significant digits; because of rounding, they may not add to totals shown. Starting with 1997, data are reported in 1-year intervals from previous years' 5-year intervals]

	1980	1985	1990	1995	1997	1998	1999	2000
Components of U.S. supply:								
Refined production ¹	27,000	22,000	18,000	10,000	20,000	22,000	20,000	23,000
Imports, unwrought, waste, and scrap ²	1,530	5,400	26,400	7,500	15,200	10,900	7,400	8,000
Imports, wrought	1,800	3,800	NA	NA	NA	NA	⁽³⁾	⁽³⁾
Sales from U.S. Government stockpile	⁽⁴⁾	—	—	—	6,550	5,110	3,850	2,840
Net deliveries from industrial stocks	NA	NA	NA	NA	NA	NA	NA	NA
Total U.S. supply⁵	30,300	31,200	44,400	17,500	41,800	38,000	31,200	33,800
U.S. germanium consumption ^{6,6:}								
Fiber optics	6,400	5,700	2,720	10,800	11,200	12,300	14,000	14,000
Catalysts	⁽⁷⁾	⁽⁷⁾	⁽⁷⁾	⁽⁷⁾	5,600	6,160	5,600	7,000
Infrared systems	12,800	24,700	20,400	4,050	2,800	3,100	4,200	4,200
Electronic and electrical	11,200	3,800	6,460	4,050	NA	4,760	2,800	1,400
Other	1,600	3,800	4,420	8,100	NA	1,680	1,400	1,400
Total U.S. consumption	32,000	38,000	34,000	27,000	28,000	28,000	28,000	28,000

¹Comprises primary and secondary production from domestic and imported ores, zinc refinery flue dust, and scrap.

²Derived from gross weight by comparing unit import value with the annual price for zone-refined metal. Does not include oxide or other compounds.

³Included in "Imports, unwrought, waste, and scrap."

⁴Stockpiling of germanium was authorized in 1984; the first purchases were made in 1987, and the first sales of surplus metal were made in 1997.

⁵Distribution of supply, except to end uses, is not attempted because export data are not available, and industrial stocks are available only for the first 2 years of the table. For the same reasons, apparent consumption cannot be calculated.

⁶Data on end-use distribution are limited. Estimates listed are based on percentage distributions obtained from producers and reported in U.S. Bureau of Mines and U.S. Geological Survey Minerals Yearbooks.

⁷Included in "Other."

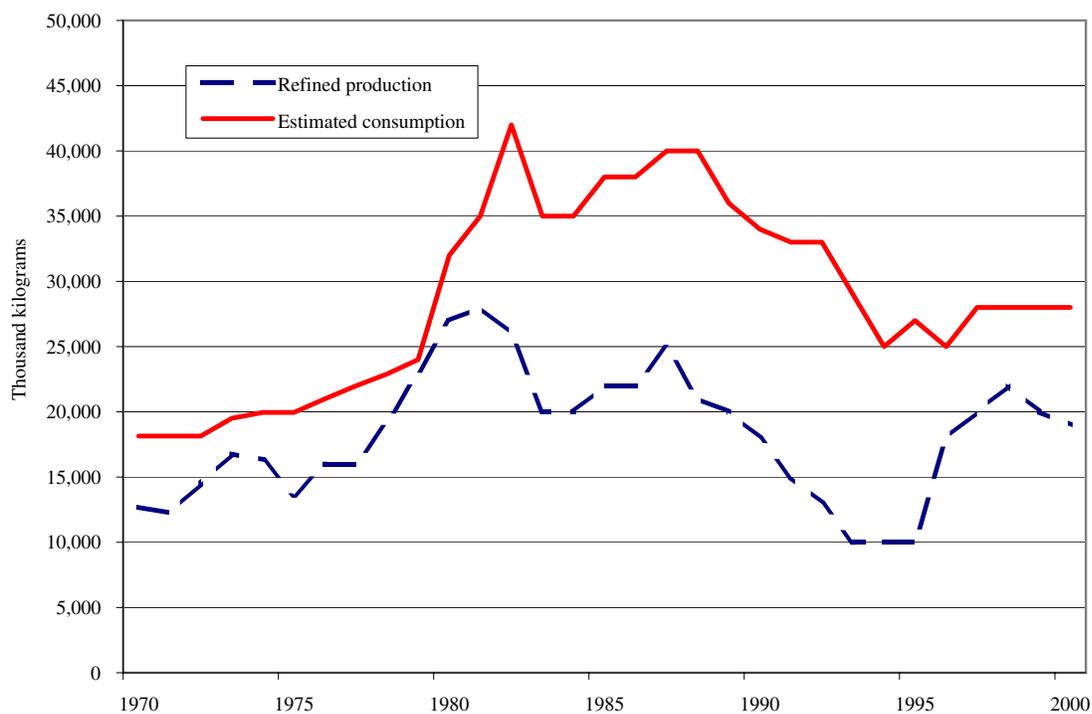


Figure 5. U.S. production and consumption of refined germanium. Data from U.S. Bureau of Mines, 1960-1994; U.S. Geological Survey, 1995-2000.

Economic Factors

Because germanium is always a byproduct, its mine and smelter costs are not usually separated from those of the principal product. The costs of its extraction from smelter residues and its subsequent refining or conversion to compounds are, of course, known to the producers but are considered to be company proprietary data and are unavailable to the public. Whether or not germanium is used in products has much more to do with its importance to product performance and to how it affects manufacturing methods than to its cost per kilogram.

U.S. mine producers are granted a 14 percent depletion allowance on their domestic and foreign production of germanium. This is a percentage of the income from mine production that is considered to be a return of invested capital and thus not subject to income tax, recognition that, when being mined, ore deposits are assets that are being depleted.

Imports into the United States of GeO₂ are subject to a duty of 3.7 percent of their value. Imports of unwrought metal are subject to a 2.6 percent duty, and imports of wrought metal, to a 4.4 percent duty. Special rates apply for some countries or regions. Waste and scrap can be imported duty-free.

Outlook

In the near term, the existing uses of germanium are likely to remain the important ones; however, their relative shares of total consumption may change. Fiber optics will remain the largest use, but in view of the overbuilding of fiber optic lines in recent years—it is estimated (Thorsen, 1997, p. 272) that 30 to 50 percent of U.S. long-distance fiber telephone lines consist of unused (“dark”) fiber—the fiber optics share of the germanium market may decline for several years. IR uses will probably grow as demand in both the military and civilian sectors increases. The use as a polyester polymerization catalyst could grow slowly if growth in PET production is sufficiently strong to outstrip the effects of new substitute catalysts and competition from the new PEN polymers. If the germanium-catalyzed process for making HFC refrigerants is commercially successful, then that segment of the catalyst market could grow rapidly. The electronics sector will probably remain small, although it should exhibit some growth as the new silicon germanium transistors and chips are increasingly used for broadband devices. Total germanium consumption is likely to remain relatively flat for the next several years.

Assuming relatively stable prices and production costs, the U.S. reserve base for germanium is adequate for at least two decades at current rates of production. The supply could be augmented, if necessary, by recovery of germanium from fly ash generated by coal-burning industrial plants and by recovery from some of the copper deposits from which germanium is not now recovered.

References Cited

- Adams, J.H., 1990, Germanium and germanium compounds, *in* Metals handbook (10th ed.): Metals Park, Ohio, ASM International, v. 2, p. 733-738.
- Adams, J.H., and Thomas, Dennis, 1994, Germanium and germanium compounds, *in* Kirk-Othmer encyclopedia of chemical technology (4th ed.): New York, John Wiley & Sons, v. 12, p. 540-555.
- Bernstein, L.R., 1985, Germanium geochemistry and mineralogy: *Geochimica et Cosmochimica Acta*, v. 49, p. 2409-2422.
- Bernstein, L.R., 1986a, Geology and sulfide mineralogy of the number one orebody—Ruby Creek copper deposit, Alaska (USA): *Economic Geology*, v. 81, no. 7, p. 1675-1689.
- Bernstein, L.R., 1986b, Renierite, Cu₁₀ZnGe₂Fe₄S₁₆•Cu₁₁GeAsFe₄S₁₆—A coupled solid solution series: *American Mineralogist*, v. 71, no. 1-2, p. 210-221.
- Brady, G.S., and Clauser, H.R., 1997, Germanium, *in* Materials handbook (11th ed.): New York, McGraw-Hill Book Company, p. 339.
- Brown, R.D., Jr., 2002, Germanium: U.S. Geological Survey Mineral Commodity Summaries 2002, p. 70-71.
- Cominco Ltd., 2000, Germanium dioxide material safety data sheet: Web site at <http://www.teckcominco.com/products/msds-germaniumdioxide-1200.pdf>. (Accessed January 11, 2002.)

- Crisp, John, 2001, *Introduction to fiber optics* (2d ed.): Oxford, United Kingdom, Newnes (An imprint of Butterworth-Heinemann), 230 p.
- Environmental News Network, 1999, Solar cell efficiency makes big leaps: Web site at <http://www.cnn.com/NATURE/9910/27/solar.cells.enn>. (Accessed April 16, 2002.)
- Greenwood, N.N., and Earnshaw, A., 1998, Germanium, tin, and lead, chap. 10 of *Chemistry of the elements* (2d ed.): Oxford, United Kingdom, Butterworth-Heinemann Publishers Ltd., p. 367-405.
- Harner, H.R., 1961, Germanium, in Hampel, C.A., ed, *Rare metals handbook* (2d ed.): New York, Reinhold Publishing Co., p. 188-197.
- Hecht, Jeff, 2002, *Understanding fiber optics* (4th ed.): Upper Saddle River, N.J., Prentice Hall, 773 p.
- IBM Microelectronics, [undated], Silicon germanium: Web site at <http://www-3.ibm.com/chips/bluelogic/showcase/sige>. (Accessed December 20, 2001.)
- Institute for Materials Research, University of Leeds, 1999, Areas of research: Web site at <http://www.materials.leeds.ac.uk/Groups/Photonics/photonic.htm>. (Accessed January 18, 2002.)
- Lucent Technologies Inc., 1997, Bell labs improves process to recover germanium: Web site at <http://www.bell-labs.com/news/1997/October/16/1.html>. (Accessed December 20, 2001.)
- Moreno, Anne-Marie, ed., 1997, *Metal traders of the world* (6th ed.): Surrey, United Kingdom, Metal Bulletin Books Ltd., 705 p.
- Moreno, Anne-Marie, ed., 2000, *Non-ferrous metal works of the world* (9th ed.): Surrey, United Kingdom, Metal Bulletin Books Ltd., 762 p.
- National Aeronautics and Space Administration, Marshall Space Flight Center, 1997, ZBLAN research takes step forward: Web site at http://science.nasa.gov/newhome/headlines/msad03jun97_1.htm. (Accessed January 25, 2002.)
- Optics.org, 2001, Scientists make polymer holey fiber: Web site at <http://optics.org/article/news/7/10/5>. (Accessed January 24, 2002.)
- Palache, Charles, Berman, Harry, and Frondel, Clifford, 1944, *Dana's system of mineralogy* (7th ed.): New York, John Wiley and Sons, v. 1, p. 386.
- Patch, Kimberly, 2001, Slimmer chips handle fast nets—Technology research news: Web site at http://www.trnmag.com/Stories/062701/Slimmer_chips_handle_fast_nets_062701.html. (Accessed February 19, 2002.)
- Plunkert, P.A., 1985, Germanium, in *Mineral facts and problems*: U.S. Bureau of Mines Bulletin 675, p. 317-322.
- Roskill Information Services Ltd., 1990, *The economics of germanium 1990* (6th ed.): London, Roskill Information Services Ltd., 175 p.
- Roskill's Letter from Japan, 1999, Germanium—Changes in the GeO₂ catalyst market: London, Roskill Information Services Ltd., July, p. 14-16.
- Roskill's Letter from Japan, 2001, Germanium—Domestic demand led by PET resin catalysts: London, Roskill Information Services Ltd., November, p. 13-14.
- Rutgers University, [undated], Non-oxide and heavy-metal oxide glass fibers: Web site at http://irfibers.rutgers.edu/ir_rev_glass.html. (Accessed January 25, 2002.)
- Scientific Instruments Inc., [undated], Germanium resistance thermometers: Web site at <http://www.scientificinstruments.com/sensors/grt.htm>. (Accessed December 20, 2001.)
- Spectrolab Inc., 2002, Spectrolab announces low-cost monitor photodetector for fiber-optic communications applications: Web site at http://www.boeing.com/new/releases/2002/q1/nr_020114s.html. (Accessed April 16, 2002.)
- Spectrum Laboratories Inc., 2001, Chemical fact sheet—Germanium: Web site at <http://www.speclab.com/elements/germanium.htm>. (Accessed December 21, 2001.)
- Stadnichenko, Taisia, Murata, K.J., Zubovic, Peter, and Hufschmidt, E.L., 1953, Concentration of germanium in the ash of American coals—A progress report: U.S. Geological Survey Circular 272, 34 p.
- Teijin Limited, 2001, Teijin develops new titanium-based polyester manufacturing catalyst technology: Web site at <http://www.teijin.co.jp/english/news/2001/ebd011203.htm>. (Accessed July 22, 2001.)
- Thorsen, Norma, 1997, *Fiber optics and the telecommunications explosion*: Upper Saddle River, N.J., Prentice-Hall, 559 p.
- Toyobo Research Center Ltd., [undated], New generation of high performance non-antimony catalyst for polyester production: Web site at <http://www.toyobo.co.jp/e/rd/catalyst/index.htm>. (Accessed July 22, 2001.)
- U.S. Bureau of Mines, 1937-1995, variously titled *Minor metals*, *Other metals*, or *Germanium*, in variously titled *Metals and minerals* or *Metals, minerals, and fuels*: U.S. Bureau of Mines Minerals yearbook 1936-1994, v. I, variously paginated.
- U.S. Bureau of Mines and U.S. Geological Survey, 1980, *Principles of a resource/reserve classification for minerals*: U.S. Geological Survey Circular 831, 5 p.
- U.S. Department of Energy, 2001, Germanium compounds as highly selective fluorination catalysts: Web site at <http://www.oit.gov/factsheets/chemicals/pdfs/germanium.pdf>. (Accessed January 15, 2002.)
- U.S. Geological Survey, 1997-2000, Germanium, in *Metals and minerals*: Minerals Yearbook, 1995-1998, v. I, variously paginated.

Weeks, R.A., 1973, Gallium, germanium, and indium, *in* Brobst, D.A., and Pratt, W.P., eds., United States mineral resources: U.S. Geological Survey Professional Paper 820, p. 237-246.

Winkler, Clemens, 1886, Germanium, Ge—A new nonmetallic element: *Berichte der Deutschen Chemischen Gesellschaft*, v. 19, p. 210-211.

Sources of Information:

U.S. Geological Survey Publications

Gallium, Germanium, and Indium. Ch. in *United States Mineral Resources, Professional Paper 820, 1973*

Germanium. Ch. in *Minerals Yearbook, v. I, annual*

Germanium. Ch. in *Mineral Commodity Summaries, annual*

Other Publications

American Metal Market, daily

Canadian Mines Handbook, 1998-1999

Engineering and Mining Journal, monthly

Metal Bulletin Monthly

Metal Bulletin, weekly

Mining Engineering, monthly

Mining Journal, weekly

Mining Record, weekly

Northern Miner, weekly

Platts Metals Week, weekly

Randol Mining Directory, 1999

Ryan's Notes, weekly

Appendix

Definitions of Reserves, Reserve Base, and Resources

The term “resources,” as applied to metals, refers to those concentrations of metal-bearing minerals in the Earth’s crust that are currently or potentially amenable to the economic extraction of one or more metals from them. “Reserves” and “reserve base” are subcategories of resources. “Reserves” refers to the in-place metal content of ores that can be mined and processed at a profit given the metal prices, available technology, and economic conditions that prevail at the time the reserves estimate is made. “Reserve base” is a more inclusive term that encompasses not only reserves proper, but marginally economic reserves and a discretionary part of subeconomic resources—“those parts of the resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics” (U.S. Bureau of Mines and U.S. Geological Survey, 1980).