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Mineral Commodity Profiles

Selenium

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OVERVIEW

Selenium, which is one of the chalcogen elements in group 16 (or 6A) of the periodic table, is a semiconductor that is chemically similar to sulfur for which it substitutes in many minerals and synthetic compounds. It is a byproduct of copper refining and, to a much lesser extent, lead refining. It is used in many applications, the major ones being a decolorizer for glass, a metallurgical additive to free-machining varieties of ferrous and nonferrous alloys, a constituent in cadmium sulfoselenide pigments, a photoreceptor in xerographic copiers, and a semiconductor in electrical rectifiers and photocells.

Refined selenium amounting to more than 1,800 metric tons (t) was produced by 14 countries in 2000. Japan, Canada, the United States, and Belgium, which were the four largest producers, accounted for nearly 85 percent of world production. An estimated 250 t of the world total is secondary selenium, which is recovered from scrapped xerographic copier drums and selenium rectifiers; the selenium in nearly all other uses is dissipated (not recoverable as waste or scrap). The present selenium reserve bases for the United States and the world (including the United States), which are associated with copper deposits, are expected to be able to satisfy demand for selenium for several decades without difficulty.

HISTORICAL BACKGROUND

Selenium was discovered in 1817 by J.J. Berzelius and J.G. Gahn, who isolated it from a red residue in sulfuric acid that had been made from pyrite mined at Fahlun, Sweden (Greenwood and Earnshaw, 1997, p. 747). It was named from the Greek word selene (moon), because of its chemical similarity to tellurium, which had been discovered a few years earlier and named from the Latin word tellus (Earth).

Although Willoughby Smith first demonstrated the photoconductive effect in 1873 in selenium metal and other properties that suggested potential uses were recognized, a century passed before a substantial commercial use was found for selenium. It was first used in volume as a glass decolorizer in place of manganese dioxide in 1915 in the United States. Manganese had become difficult to obtain from Russia, which was the largest mine producer, because of World War I. Commercial production of selenium in the United States, however, had begun a few years earlier with the extraction of 5t of selenium from copper refinery anode slimes in 1910; apparently most of it was used as a pigment for red glass and ceramic glazes (Hess, 1911). By 1918, annual domestic production had risen to 50 t to fill the new use as a decolorizer. Although glass decolorizing remained the principal domestic use of selenium in the years that followed the restoration of peace, the glass industry could not absorb all the selenium available from copper electrorefining, so part of the selenium-containing anode slimes from the refining cells was stockpiled during the interwar years. When the market for selenium grew larger in the 1940s, the stockpiled anode slimes were gradually processed.

Cadmium sulfoselenide (CdSSe) pigments came onto the market in artists' paints in the first decade of the 20th century. Because they were costly, expansion into a larger market awaited the development of coprecipitation with barium sulfate and zinc sulfide in the late 1920s, to create the more-economical cadmium lithopone pigments (ZnS-CdSSe-BaSO₄). In the post-World War II years, the burgeoning plastics industry provided the principal market for durable, light-fast cadmium sulfoselenide pigments. In the 1990s, however, these pigments were being phased out of some uses in response to the public's concern about toxic cadmium in the environment (Herron, 1992, p. 772).

The selenium rectifier, which was invented in 1933, was used extensively from the 1940s through the 1960s. Its use peaked (at least in terms of numbers of units) in the 1950s when it was used extensively in the power supplies of radio and television sets, and also came to be used for high-current uses, such as direct current arc welding. It remains in use today in diminished but still substantial numbers.

The first commercial xerographic document copier, which depended on the photoconductive property of selenium for its operation, came onto the market in 1959. These plain-paper copiers quickly became ubiquitous in the work place and became the largest use for selenium. In the 1990s, selenium photoreceptors were largely phased out of new copiers and replaced by organic compounds and amorphous silicon. Thus, the current xerographic market is a replacement market.

The U.S. Bureau of Mines (USBM) began publishing figures in its Minerals Yearbook on the domestic refinery production of selenium in 1940, on world refinery production in 1956, and on the end-use pattern of the domestic selenium market in 1970. Domestic production, which was about 150 t in 1940, rose gradually and peaked at 565 t

in 1969. It fell through the 1970s, then stabilized at an intermediate level in the 1980s and early 1990s before rising again in the middle 1990s (fig. 1). Domestic apparent consumption (calculated as refinery production plus net imports plus/minus stock changes) generally paralleled the course of production.

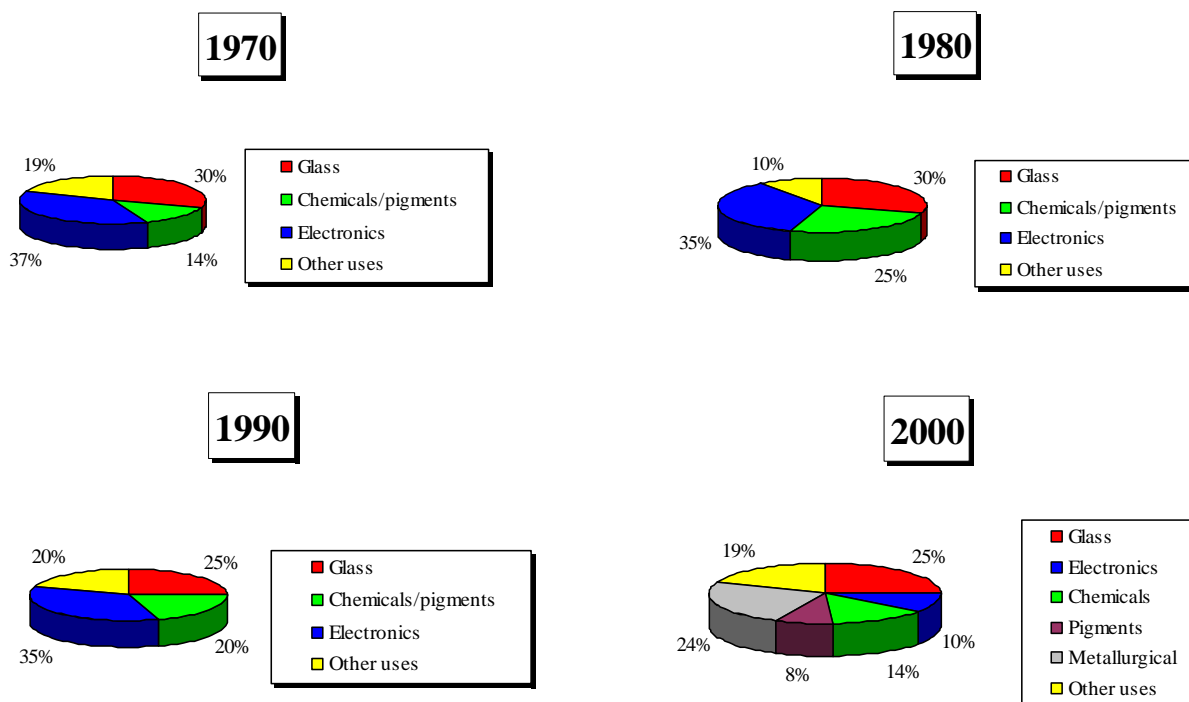


Figure 1. Pattern of U.S. selenium use, 1970–2000. [U.S. Bureau of Mines (1970–1990); U.S. Geological Survey (2000)]

DESCRIPTION

SALIENT FACTS

In the periodic table, selenium is element number 34, atomic weight 78.96, and electron configuration $[\text{Ar}]3d^{10}4s^24p^4$ and is located in period 4, group 16 (or 6A). The top two elements in group 16, oxygen and sulfur, are nonmetallics and insulators; the next two, selenium and tellurium, are semiconductors (Greenwood and Earnshaw, 1997, p. 754). Selenium's principal oxidation states are +6, +4, -2, and 0; in addition, +1, +2, +3, and +5 have been observed in the laboratory. Terrestrial selenium is a mixture of six isotopes having the following weight abundances: ^{74}Se (0.89 percent); ^{76}Se (9.36 percent); ^{77}Se (7.63 percent); ^{78}Se (23.78 percent); ^{80}Se (49.61 percent); and ^{82}Se (8.73 percent). The first five are stable isotopes, but ^{82}Se is actually a radioactive isotope with an extraordinarily long half-life of 1.08×10^{20} years. In addition, 27 radioisotopes with half-lives that range from milliseconds to more than a million years have been identified (Resource-World Net, undated).

Several allotropes of selenium exist; five are recognized in this report, but as many as eight have been claimed in the literature. The metallic gray stable form crystallizes in the hexagonal system. It is brittle and has a Mohs hardness of 2, a specific gravity of 4.79, and a melting point of 221°C . The other forms are metastable and can be converted into the stable hexagonal form by heating or chemical reaction. They include two deep-red crystalline monoclinic forms and two amorphous forms, one red, and one black. The several allotropes consist of covalently bonded rings and/or helical chains of selenium atoms (Greenwood and Earnshaw, 1997, p. 751; Hoffmann and King, 1997, p. 686).

Chemically, selenium is very similar to sulfur. Many of its compounds are analogs of sulfur compounds, and it substitutes for sulfur in minerals and other compounds.

Electrically, selenium is a p-type semiconductor. It exhibits photovoltaic action (the conversion of light to electric current) and photoconductivity (the variation of electrical conductivity with the intensity of light incident on the semiconductor).

PRINCIPAL FORMS, ALLOYS, AND COMPOUNDS

Selenium is a highly reactive element. It forms “more than 170 solid compounds, three liquid compounds (Se_2Cl_2 , SeF_4 , and CSe_2), and two gaseous compounds (H_2Se and SeF_6)” (Chizhikov and Shchastlivyi, 1968, p. 142). Of the inorganic compounds, the most important classes are the selenides (58 formed with metals and 8 with nonmetals), halides, oxyhalides, oxides, acids, and salts of the oxyacids. The organic compounds include a large number of selenium analogs of organosulfur compounds. Biologically important organics include selenocysteine, “seloaminocarboxylic acids, selenium peptides, and selenium derivatives of pyrimidines, purines, cholines, steroids, coenzyme A, and other compounds” (Hoffman and King, 1997, p. 702). Some of the more commonly used selenium compounds are shown in table 1.

Table 1. Selected commonly used selenium compounds.
[Hoffmann and King, 1997, p. 698]

| Compound | Formula | Compound | Formula |
|-------------------------|--------------------------|---------------------------------|-----------------------------------------------------|
| Barium selenite | BaSeO_3 | Selenium diethyldithiocarbamate | $[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_4\text{Se}$ |
| Barium selenate | BaSeO_4 | Selenium dioxide | SeO_2 |
| Cadmium sulfoselenide | CdSSe | Selenium disulfide | SeS_2 |
| Calcium selenite | CaSeO_3 | Selenium oxychloride | SeOCl_2 |
| Ferroselenium | FeSe | Selenium tetrachloride | SeCl_4 |
| Nickelselenium | NiSe | Selenourea | $(\text{NH}_2)_2\text{CSe}$ |
| Potassium selenocyanate | $\text{K}(\text{SeCN})$ | Sodium selenate | Na_2SeO_4 |
| Selenic acid | H_2SeO_4 | Sodium selenide | Na_2Se |
| Selenous acid | H_2SeO_3 | Sodium selenite | Na_2SeO_3 |

COMMERCIAL GRADES, SHAPES, AND SPECIFICATIONS

Selenium is sold in four grades. Commercial refined selenium is 99.5 weight percent minimum selenium, and is marketed mainly as powder, although granules and lump are available. Pigment grade is 99.7 weight percent minimum selenium. High grade is 99.999 weight percent minimum selenium, with deleterious impurities such as arsenic, iron, mercury, and tellurium below 1 to 2 parts per million (ppm). It is sold as shot or powder. Ultrahigh grade is 99.999 to 99.9999 weight percent selenium (Hoffmann and King, 1997, p. 705). The industry has no specifications for the several grades, but some producers supply their own specifications to customers.

SOURCES OF SELENIUM

PRIMARY SELENIUM, GEOCHEMISTRY

Selenium is extensively associated in nature with sulfur. Because the radius of the Se^{2-} anion is only a little larger (8 percent) than that of the S^{2-} anion, selenium substitutes readily for sulfur in the structures of sulfide minerals (McNeal and Balistreri, 1989, p. 5). It is introduced to the crust by way of igneous intrusions, in which it is a constituent of a wide array of sulfide minerals, and by volcanism when it is vented as gaseous SeO_2 and H_2Se and also trapped in volcanic glasses at concentrations up to several hundred parts per million. Its mean concentration in sulfide minerals, 0.05 ppm, has been taken to be representative of its crustal abundance (Lakin and Davidson, 1973). Other estimates of crustal abundance have ranged from 0.03 to 0.08 ppm (Spectrum Laboratories, undated).

Some representative selenium contents in crustal materials, in parts per million, are as follows: igneous rocks, 0.05; sandstones, 0 to 0.5; shales, 0 to 0.6; limestones, 0.08; and soils, 0.2 (Spectrum Laboratories, undated). The

selenium content, however, can vary greatly from one rock or soil type to another. Because sulfur is much more soluble than selenium in aqueous environments, the two elements tend to separate during the weathering that is a precursor to the formation of sedimentary rocks. For this reason, selenium is largely absent from deposits of sulfates and some types of sulfur deposits. Although selenium plays no role in plant nutrition, it is taken up by plants and thus concentrated where organic matter is concentrated; for example, in coals and black shales where it is often associated with iron pyrite. Black shales may contain as much as 20 ppm selenium regionally and up to 1,500 ppm locally. Domestic coals average 1.5 ppm selenium, and coals generally contain from 0.5 to 12 ppm selenium (Hoffmann and King, 1997, p. 689). Crude oil generally contains less than 0.5 ppm selenium. Seawater is estimated to contain only 0.5 part per billion (ppb) selenium, and drinking water usually contains less than 1 ppb.

PRIMARY SELENIUM, GEOLOGY

Primary selenium is produced entirely as a byproduct of base-metal mining and processing. More than 90 percent of it is derived from copper ores, and most of the other 10 percent, from lead ores. There are no selenium ores or ore deposits, but selenium is present as a minor constituent in scores of minerals, most of them sulfides. Although selenium is, with respect to commercial exploitation, a dispersed element, it is also capable of forming a substantial number of minerals in which it is a main component; thus, geochemically, it has aspects of being both a dispersed and a mineral-forming element. Sindeeva (1964, p. 35-37) provided chemical formulas for 36 minerals that can be called selenium minerals; that is, minerals in which selenium is a main component. A few of the better known examples, all selenides, are crookesite, $(\text{Cu,Tl,Ag})_2\text{Se}$; clausthalite, PbSe ; eucairite, CuAgSe ; and naumannite, Ag_2Se (Stone and Caron, 1961). The selenium reserve and reserve base figures published by the U.S. Geological Survey (USGS) exclude selenium in lead ores and other mineral deposits and are based solely on reserves and reserve base estimates for the main source of selenium, copper ores (table 2). The part of copper resources that appears likely to be processed by leaching/electrowinning is discounted because these methods do not recover selenium. The selenium estimates take into account typical recoveries of selenium per metric ton of primary electrolytically refined copper; only a part of the selenium content of anode slimes is recovered. The estimates are derived from the copper resource figures by using the recovery factor 0.215 kilogram of selenium per metric ton of primary electrolytic copper recoverable from the resources; for Canada, where the selenium contents of copper ores are higher, the factor 0.64 kilogram per metric ton is used (Brown, 1995). No estimate is available for total selenium resources, but coal deposits have been estimated to contain from 80 to 90 times more selenium than do copper deposits. Recovery of selenium from coal is considered to be unlikely in the foreseeable future. (See Appendix for definitions of reserves and reserve base.)

Table 2. Selenium reserves and reserve base, yearend 2001. [In metric tons, recoverable selenium. All data are rounded to two significant digits; because of independent rounding, they may not add to totals shown]

| Country | Reserves | Reserve base |
|-----------------|----------|--------------|
| Chile | 16,000 | 37,000 |
| Canada | 6,400 | 15,000 |
| Peru | 5,400 | 9,300 |
| United States | 4,600 | 9,200 |
| Zambia | 3,500 | 6,500 |
| Other countries | 48,000 | 90,000 |
| World totals | 84,000 | 170,000 |

SECONDARY SELENIUM

About 90 percent of the selenium consumed domestically is dissipated into the environment and, therefore, is not recoverable. The selenium contents of glass and free-machining alloys are not accounted for during recycling of those materials and are probably volatilized during melting operations. Selenium pigments, fertilizers, animal feeds, chemicals, and pharmaceuticals are dissipated. That leaves electronic uses as the possible source of scrap and, in fact, a high percentage of the selenium used in document copiers and laser printers and possibly some of that used in

rectifiers is recovered and reprocessed into secondary selenium. At the current rate of consumption, this means that no more than about 10 percent of annual domestic consumption, or 50 t, is recovered as secondary selenium.

PRODUCTION TECHNOLOGIES

PRIMARY SELENIUM

Copper refinery anode slimes, which are the source of more than 90 percent of the selenium produced, usually contain from 5 to 25 weight percent selenium often as the selenides of silver (Ag_2Se); copper ($\text{Cu}_{2-x}\text{Se}_x$, where x is less than 1; and copper-silver (CuAgSe). Lead refinery residues generally contain lesser quantities of selenium and are sometimes processed together with copper slimes. The primary commercial objective in processing the slimes is to recover precious metals; the recovery of selenium and tellurium is a secondary goal. Processing begins with the removal of most of the copper by a sulfuric acid leach. Selenium, tellurium, and the precious metals are then extracted from the decopperized slimes.

The description below covers only the extraction of selenium and tellurium.

In outline, the processing proceeds as follows:

Selenium is extracted in compound form from the decopperized slimes and concurrently separated from tellurium and from impurities.

The selenium is reduced to elemental selenium.

The elemental selenium is purified.

Step 1 is usually accomplished by one of the following methods: soda ash roasting, sulfation roasting, chlorination, or copper-lead slimes treatment.

EXTRACTION

Soda Ash Roasting

Decopperized slimes are mixed with sodium carbonate, a binder clay, and water to form a paste, which is then pelletized, dried, and roasted at a low temperature ($530^\circ\text{-}650^\circ\text{C}$) to convert all selenium and tellurium to the soluble hexavalent state. The roasted pellets are ground and leached with water. Whereas the selenium goes into solution (as the selenate Na_2SeO_4), the tellurium is insoluble in the alkaline solution; thus, the two elements are separated in this stage. The sodium selenate is then precipitated from solution, mixed with charcoal, and heated to convert it to the selenide Na_2Se . The selenide is leached with water and then oxidized by blowing air through the solution to precipitate elemental selenium (Hoffmann and King, 1997, p. 690-692).

Sulfation Roasting

Dried decopperized slimes are roasted with sulfuric acid at 500° to 600°C to convert the selenium and tellurium to their dioxides. Selenium dioxide volatilizes at these temperatures and is collected from the off-gases, whereas tellurium dioxide remains in the slimes. In the off-gas water scrubber where the temperature is lower, the oxidation reaction reverses; that is, the selenium dioxide reacts with water and sulfur dioxide to form sulfuric acid and elemental selenium.

Wet Chlorination

Decopperized slimes are slurried in hydrochloric acid or water heated to about 100°C . Chlorine and oxidizers, such as sodium chlorate or hydrogen peroxide, which liberate chlorine from the acid, are bubbled through the slurry. Selenium, tellurium, the precious metals, and several other metallic impurities go into solution as chlorides. Selenium and the precious metals are selectively precipitated from solution by sulfur dioxide. Selenium is recovered and simultaneously separated from the precious metals by vacuum distillation (Hoffmann and King, 1997, p. 694-696).

Copper-Lead Slimes Treatment

Copper slimes and lead slimes are sometimes treated together. They are mixed with lead materials, which provide a low melting temperature; selenium is volatilized by blowing air into the molten lead mixture and is then recovered from stack gases at the scrubbers.

PURIFICATION

At least three methods have been used to separate selenium from its main impurity (tellurium) and several lesser impurities. The first method is based on the greater volatility of selenium compared with tellurium. Thus, selenium may be vacuum distilled at a temperature range of from 300° to 400° C or distilled at atmospheric pressure at a higher temperature. In the second method, selenium is heated at about 300° C with a flux of mixed sodium and potassium nitrates. The selenium and precious metal impurities do not react with the flux, whereas the tellurium and some of the other impurities are absorbed into the flux. If precious metals impurities are a problem, then a further step is required to separate them from the purified selenium. In the third method, selenium is dissolved in hot sodium sulfite solution to form sodium selenosulfite, while tellurium remains undissolved. The hot solution is filtered, and as it cools, the reaction reverses, to yield sodium sulfite and purified elemental selenium (Hoffmann and King, 1997, p. 696-697).

SECONDARY SELENIUM

Nearly all secondary selenium, which may be as little as 100 metric tons per year (t/yr) worldwide, is recovered from xerographic photocopier drums. The selenium layer is either broken up mechanically, then cleaned and remelted; or dissolved in sodium sulfite or other solvents and then precipitated (Roskill Information Services, 1988, p. 6).

USES

According to circumstance, selenium is a conductor and a nonconductor, an oxidizer and a deoxidizer, a colorant and a decolorant, crystalline and amorphous. These diverse characteristics have led to the development of a wide array of uses for the element.

The usage figures published for selenium have some considerable limitations. Percentage breakdowns for the annual consumption of selenium in its principal end use categories in the United States have been published in USBM and USGS commodity statistics since 1970. They are estimates, obtained not by formal surveys of industry, but by contact with persons in the producing industry and a trade association. In recent years, the categories have been increased from four to six to provide more detail. How faithfully these percentages represent the U.S. consumption pattern, as distinct from the world pattern, is not clear. Further, to estimate tonnages, a calculated apparent consumption that is approximate because of the lack of data for exports (before 1972) and for industry stocks must be used.

The four categories described in this section are those that have been in print since 1970. They are used in figure 1, which shows shifts in the use pattern during the past three decades. The chart for 2000 in the figure shows the pattern by use of six categories, chemicals and pigments having been separated, and metallurgical uses extracted from the other uses category. In table 3, the four-category pattern ("U.S. consumption pattern for selenium") is tracked in terms of tonnage.

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

[In metric tons. NA, Not available. W, Withheld to avoid disclosing company proprietary data. -----, Zero. Data include estimates. All data are rounded to three significant digits; because of independent rounding, they may not add to totals shown. Note change at 1995 from 5- to 1-year intervals]

| | 1960 | 1965 | 1970 | 1975 | 1980 | 1985 | 1990 | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 |
|------------------------------------------------------|------------|------------|------------|------------|------------|-------------------------|------------|------------|------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Components of U.S. supply: | | | | | | | | | | | | | |
| Refined production: | | | | | | | | | | | | | |
| Primary ¹ | 244 | 231 | 456 | 162 | 141 | W | 287 | 373 | 379 | W | W | W | W |
| Secondary | ----- | 14 | 14 | 9 | 45 | W | NA | NA | NA | NA | NA | NA | NA |
| Imports for consumption ² | 73 | 114 | 206 | 403 | 284 | 401 | 383 | 324 | 428 | 346 | 339 | 326 | 476 |
| Sales from U.S. stockpile | ----- | ----- | ----- | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Net deliveries from industrial stocks | 30 | 129 | 23 | ----- | 54 | W | 47 | NA | NA | NA | NA | NA | NA |
| Total U.S. supply | <u>347</u> | <u>488</u> | <u>699</u> | <u>577</u> | <u>524</u> | <u>NA</u> | <u>717</u> | <u>697</u> | <u>807</u> | <u>NA</u> | <u>NA</u> | <u>NA</u> | <u>NA</u> |
| Distribution of U.S. supply: | | | | | | | | | | | | | |
| Exports ⁴ | ----- | 45 | 171 | 54 | 82 | 154 | 207 | 269 | 322 | 127 | 151 | 231 | 82 |
| Purchases for U.S. stockpile | ----- | 8 | ----- | ----- | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Net additions to industrial stocks | ----- | ----- | ----- | 33 | ----- | W | NA | NA | NA | NA | NA | NA | NA |
| Apparent consumption | <u>324</u> | <u>434</u> | <u>528</u> | <u>490</u> | <u>388</u> | ⁵ <u>477</u> | <u>510</u> | <u>517</u> | <u>564</u> | ⁵ <u>509</u> | ⁵ <u>478</u> | ⁵ <u>383</u> | ⁵ <u>504</u> |
| Total distribution of supply | <u>324</u> | <u>487</u> | <u>699</u> | <u>577</u> | <u>470</u> | <u>631</u> | <u>717</u> | <u>786</u> | <u>886</u> | <u>636</u> | <u>629</u> | <u>614</u> | <u>586</u> |
| U.S. consumption pattern for selenium ⁶ : | | | | | | | | | | | | | |
| Glass ⁷ | NA | 159 | 173 | 138 | 116 | 143 | 128 | 119 | 141 | 127 | 120 | 96 | 126 |
| Chemicals and pigments | NA | 78 | 63 | 92 | 97 | 119 | 102 | 109 | 130 | 112 | 105 | 84 | 111 |
| Electronics | NA | 152 | 232 | 201 | 136 | 167 | 178 | 109 | 90 | 71 | 57 | 42 | 50 |
| Other uses ⁸ | NA | 45 | 60 | 59 | 39 | 48 | 102 | 180 | 203 | 199 | 196 | 161 | 217 |
| Total apparent consumption | <u>324</u> | <u>434</u> | <u>528</u> | <u>490</u> | <u>388</u> | <u>477</u> | <u>510</u> | <u>517</u> | <u>564</u> | <u>509</u> | <u>478</u> | <u>383</u> | <u>504</u> |

¹Prior to 1981, production and stocks included net production of granular selenium, a semirefined form of selenium.

²Unwrought metal, waste and scrap, and selenium compounds.

³The U.S. Government stockpile had been liquidated by 1976.

⁴Unwrought metal, waste and scrap.

⁵Calculated by using an estimate for shipments to consumers.

⁶All end use consumption figures are estimates; those for 1985 and from 1997 to 2000 are by the authors of this report and based on estimated apparent consumption.

⁷Includes glass frit used for surface pigmentation of ceramic products.

⁸Comprises agricultural, metallurgical, and miscellaneous uses.

GLASS

Selenium is used to decolor some glasses, to color other glasses, and to color the vitreous glazes that are used to coat some ceramic products.

A few hundredths of a percent of iron in mixed ferrous and ferric oxidation states is present as an impurity even in the high-grade sand used for silica glass and imparts a muddy color to the raw glass. Oxidizers, such as arsenic trioxide, are added to the melt to reduce the population of ferrous ions; the product is a glass that has a pale-yellowish-green color. Selenium, as elemental selenium, barium selenite (BaSeO₃), or sodium selenite (Na₂SeO₃), is then added to the melt to remove the remnant color, thus yielding a clear colorless glass, most of which is used as

container glass. Depending on the iron content of the glass, from 10 to 30 grams (g) of selenium per metric ton of glass is added. Only about 20 percent of this is retained in the glass; the remainder volatilizes from the melt. Used along with cobalt oxide, ferric oxide, and cadmium sulfide, selenium, at a concentration of about 1 kg/t, is a decolorizer for the neutral gray heat absorbent flat glass used in automobile windows and the windows of modern office buildings. Additions of selenium with cobalt oxide or iron oxide are used to produce black or bronze-colored architectural glass. Glass is colored pink by the addition of from 0.05 to 1 percent selenium to the melt under oxidizing conditions. Various combinations of selenium oxide with the oxides of antimony, arsenic, bismuth, cobalt, or iron yield black, purple, or yellow glasses. Selenium, silicon, and a variable third additive yield other colors, such as amber, emerald, and topaz. Selenium is used with cadmium sulfide to produce glasses that range in color from orange-yellow to ruby red. To make ruby glass, selenium (up to 1 percent) and cadmium sulfide (up to 2 percent) are added to the melt under reducing conditions. The glass is cooled quickly then heated and held until tiny cadmium sulfoselenide crystals, which act as the color centers, precipitate throughout the glass. Ruby glass of this composition is characterized by good transmission of red light and sharp spectral cut-off. It is widely used for the lenses in traffic signal and navigation lights.

Powdered or granulated glass, which is called frit, is commonly fused onto the surfaces of ceramic products to seal and color them. Frit that contains cadmium sulfoselenide is used to impart brilliant surface colors that range from yellow through red and maroon to certain ceramic products. The color produced is a function of the ratio of sulfur to selenium in the compound; the more selenium, the redder the color (Hoffmann and King, 1997, p. 711-712; Roskill Information Services Ltd., 1988, p. 56-59).

Zinc and cadmium selenide glasses, which readily transmit infrared radiation, are used in lenses for industrial carbon dioxide lasers.

CHEMICALS

Selenium, selenium dioxide, and other selenium compounds are used as catalysts or oxidizing agents in many organic chemical processes, such as oxidation, hydrogenation, dehydrogenation, isomerization, and polymerization. Some examples of common applications are noted below (Roskill Information Services Ltd., 1983, p. 63):

Oxidation of olefins to olefin oxides and unsaturated aldehydes; oxidation of alkyl aromatics to aromatic acids; oxidation of ketones to branched or cyclic ketones; and oxidation of acetaldehyde to acetic acid.

Use of selenium as a promoter in the reformation of naphtha.

These and the many other specific process applications together account for about two-thirds of the selenium used in the chemicals and pigments category.

PIGMENTS

Nearly all the pigments in which selenium is used are cadmium sulfoselenide pigments. These range from yellow to maroon in color according to the relative proportions of contained sulfur and selenium. They are brilliant, highly resistant to light and chemical attack, stable to high temperatures, and highly opaque (Hoffmann and King, 1997, p. 712). By far their largest use is in the coloring of plastics, especially the types that are processed and used at relatively high temperatures, such as high density polyethylene, acrylonitrile-butadiene-styrene, and polypropylene (Roskill Information Services Ltd., 1988, p. 61). Because they are expensive pigments, they are reserved for use in plastics processed at temperatures of up to 400° C and for plastic products used in high-temperature environments (up to 500° C) when it is important to avoid deterioration of the color, especially if the color is part of a visual safety code, such as might be used for cable coverings, steam line coverings, and other products.

Relatively small amounts (less than 10 percent of the total market) of cadmium sulfoselenide pigments are used in specialized paints and coatings and in the manufacture of ceramic goods. The application of selenium-containing pigments to ceramics by use of glass frit was mentioned in the discussion of glass manufacture. Another way of applying cadmium sulfoselenide pigments to ceramics is to encapsulate the pigment grains in zirconia (ZrO₂). The zirconia protects the pigment, which allows it to survive high firing temperatures.

Cadmium sulfoselenide pigments contain a highly toxic element, cadmium, whose use has been discouraged in the past two decades or more. Primarily for this reason, use of these pigments fell rapidly in the first half of the 1990s as manufacturers developed reasonably satisfactory substitutes (Novotny, Solc, and Trojan, 1995, p. 31). In

the United States, the rapid decline in consumption of selenium in cadmium sulfoselenide pigments appears to have been slowed in the latter half of the 1990s.

Other important selenium-containing pigments include the zinc-chromium-selenate pigments that are used to protect metal surfaces against corrosion.

ELECTRONICS

The consumption of selenium for use in rectifiers, xerographic photoreceptors, photovoltaic cells and photoconductive cells has been reported in a single category (“electronics”) in USBM and USGS publications. Through the 1940s, 1950s, and at least part of the 1960s, the use in selenium rectifiers dominated the category. With the appearance in 1959 of the first commercially successful xerographic photocopier, the predominance of the selenium rectifier in the electronics category began to wane, and from sometime in the 1960s until today, the photoreceptor use has dominated the category. The advent in 1984 of the laser printer, which operates in a way similar to that of a xerographic copier, helped insure that dominance.

RECTIFIERS

The basic component of the selenium rectifier is a steel or aluminum plate coated with a 1-micrometer (μm) film of nickel or bismuth, which is used as one electrical contact upon which a 50 to 60 μm layer of halogen-doped selenium is deposited; this, in turn, is covered with a film of cadmium alloy, which is used as the other electrical contact. The selenium layer is converted into polycrystalline gray (hexagonal) selenium by annealing.

The metal plate configuration lends itself to stacking, which makes these rectifiers suitable for high-voltage, as well as low-voltage power supplies. They have a high (85-percent) working efficiency and are more durable and reliable than competitor rectifiers. This reliability is a factor that, in some end uses, is of more importance than the lower cost of some competitors, such as silicon rectifiers. Although they have been largely supplanted by the lower cost silicon diode, they still have niche markets in such devices as arc welders, electrostatic air cleaners, and some kinds of transformers.

XEROGRAPHIC COPIERS

The xerographic process was demonstrated in the late 1930s, using sulfur as the photoreceptor. The photoreceptor material must be an insulator in the dark and a conductor when exposed to light. In xerographic plain-paper copiers, the photoreceptor material is present as a 50- to 60- μm layer on a drum or belt. It is electrostatically charged and then exposed to the image. Where the image is light, the photoreceptor becomes a conductor, thus allowing the charge to dissipate; where the image is dark, the charge remains. Oppositely charged toner powder is then introduced to the photoreceptor surface but clings only to the dark areas of the latent image. The adhering toner is then transferred to charged plain paper and fixed in place by heating to form a permanent copy of the original document. Amorphous (glassy) selenium, which was found to be a photoconductor in the late 1940s, was the photoreceptor in the first commercial photocopiers. It was largely satisfactory, but it tended to crystallize and was easily scratched; consequently, it had to be replaced frequently. More-durable and photosensitive coatings were then developed, which used arsenic-stabilized selenium, selenium-tellurium alloys (4 to 13 percent tellurium), or arsenic triselenide (As_2Se_3). Very large numbers of copiers and laser printers that use selenium-based photoreceptors are still in use, but in copiers produced during the past few years, selenium has been displaced by several competitor materials. Amorphous silicon has displaced selenium to some extent in high-speed heavy-duty copiers, and organic photoreceptors have largely replaced selenium in low-speed and personal copiers, as well as in color copiers (Hoffman and King, 1997, p. 708-709; Roskill Information Services Ltd., 1988, p. 46-53).

PHOTOCELLS

Selenium has been used in some kinds of photovoltaic cells—devices that convert light energy into electrical energy. The selenium photovoltaic cell is similar in construction to a rectifier plate except that the cadmium electrode layer is replaced by a transparent layer of cadmium oxide for the admission of light. It has a spectral response similar to that of the human eye, making it useful as a photographic photometer. It has, however, been largely displaced from this use by the cadmium sulfide photoconductive cell. Copper indium diselenide (CuInSe_2) is

one of three semiconductor materials that have been used for thin film solar photovoltaic cells. Most solar photovoltaics in use, however, use crystalline silicon and are not of the thin film type (U.S. Department of Energy, 2002).

The selenium photoconductive (or photoelectric) cell typically consists of a thin layer of selenium on a metal substrate, covered by a thin translucent film of gold. Light incident on the cell increases its conductance by as much as 1,000-fold, making it useful in a variety of light-sensing devices, such as electric eyes and photometers. Most photoconductive cells, however, use silicon or cadmium sulfide as the photoconductive material (Roskill Information Services Ltd., 1988, p. 56).

METALLURGICAL USES

Selenium is often added in small amounts to ferrous and copper-based metals. The principal reason for adding selenium is to enhance machinability, which enables faster production with better surface finish. The addition of from 0.04 to 0.08 percent selenium with somewhat larger quantities of lead to low-carbon steels more than doubles the machinability. The addition of at least 0.15 percent selenium to series 302 and 430 stainless steels improves machinability markedly, as does the addition of from 0.025 to 1 percent selenium to copper and its alloys. Selenium is the only additive that is suitable for improving the machinability of cobalt-iron and nickel-iron alloys used in electrical equipment. The use of selenium in copper alloys has become potentially important in the past decade because it has been demonstrated to work well with bismuth in improving the machinability of the new environmentally friendly lead-free brasses that are being introduced into plumbing hardware.

Selenium also serves in steel as a deoxidizer and grain refiner, and in stainless steels acts to prevent porosity. Additions of less than 0.1 percent selenium to the silicon steel used in transformer cores alters the microstructure in a way that improves the steel's magnetic properties. Selenium acts as a grain refiner in the antimonial lead used in the grids and cell connectors of some types of lead-acid batteries.

Selenium compounds added to chromium-plating electrolytes impart a more-uniform protection against corrosion by inhibiting localized corrosion of the plated steel article. The trade-off is a less reflective plated surface, which may or may not be considered less desirable than a mirror finish. In friction brake linings, the presence of selenium in copper particles substantially improves their adherence to nonmetal particles in the pressed and sintered lining material (Hoffmann and King, 1997, p. 710-711).

Sulfur competes with selenium as an additive to steel to improve machinability but tends to have a more-deleterious effect on certain properties of the steel, such as corrosion resistance, cold working characteristics, and strength. Tellurium is generally used to improve machinability in copper alloys in preference to selenium on the basis of cost.

OTHER USES

MEDICAL USES

The principal use of selenium in medicine is associated with its role in animal and human nutrition. Selenium is an essential micronutrient for animals and humans. Food plants grown on most soils contain sufficient selenium to satisfy nutritional requirements. In some parts of the world, such as in regions of China, Denmark, Finland, New Zealand, and parts of the Eastern and Northwestern United States, however, the soils are deficient in selenium (Mikkelsen, Page, and Bingham, 1989, p. 83; Mayland, 1994, p. 33). To prevent white muscle disease and other selenium-deficiency disorders in domestic animals in these regions, selenium is added to fertilizers and/or added to animal feed as a supplementary nutrient. In the United States, about 50 t/yr of selenium is used for direct animal feed supplementation (Oldfield, 1998, p. 136).

For humans, the minimum dietary requirement is about 55 micrograms per day ($\mu\text{g}/\text{d}$), and the normal intake in the United States from food is believed to be in the range of 70 to 150 $\mu\text{g}/\text{d}$ (ATSDR, 1997). Selenium, however, becomes toxic at levels not far above the usual intake. About 400 $\mu\text{g}/\text{d}$ is considered to be the maximum safe intake, and the maximum to be derived from separate selenium supplements is put at 200 $\mu\text{g}/\text{d}$. Because food for a largely urban population, such as in the United States, comes from a wide assortment of places around the country and the world, each with its own distinct soils, calculating one's daily selenium intake from food is difficult to impossible. For this reason and the narrow therapeutic window, some medical professionals do not recommend separate

selenium supplements for the general populace (UC Berkeley Wellness Letter, 2000). Others, not always medical professionals, feel that the claimed benefits of selenium in combating diseases, such as arthritis, heart disease, cancer, and HIV/AIDS, warrant the supplementation of diet with up to 100 to 200 $\mu\text{g}/\text{d}$ of selenium. In any case, some people with severe gastrointestinal disorders and those completely dependent on intravenous feeding (total parenteral nutrition) require supplementation of dietary selenium (NIH Clinical Center, 2001).

Selenium disulfide in a stabilized buffered suspension is the active ingredient in a well-known antidandruff shampoo.

The least abundant of the six naturally occurring isotopes of selenium, ^{74}Se , has been used to track the movement of selenium through body tissues.

MISCELLANEOUS USES

Selenium has a wide variety of miscellaneous uses, a few of which are cited below.

Dialkylselenides are used as oxidation inhibitors in petroleum lubricants.

The barium, calcium, and zinc salts of selenic acid augment the detergency of lubricating oils.

Powdered selenium and selenium diethyl dithiocarbamate are used as accelerators of vulcanization of low-sulfur natural and synthetic rubbers.

Selenium compounds are used as antioxidants, bonding agents, and polymerization agents in rubber.

Sodium selenite is used in photography to produce sepia tones.

Sodium selenite has been used to reduce the amount of mercury in lake water. Released slowly into the lake, it reacts with mercury compounds in the water to form an insoluble precipitate of mercury selenide that falls to the bottom. The mercury is thus removed from the aquatic food chain.

TRENDS IN USE

Data on total world consumption are not available. However, inspection of a plot of world refinery production, considered as a proxy for world consumption, shows slow, but steady growth over the 44 years from 1956 through 2000 for which data are available (fig. 2). The compound rate of growth during the period averaged about 2.5 percent per year.

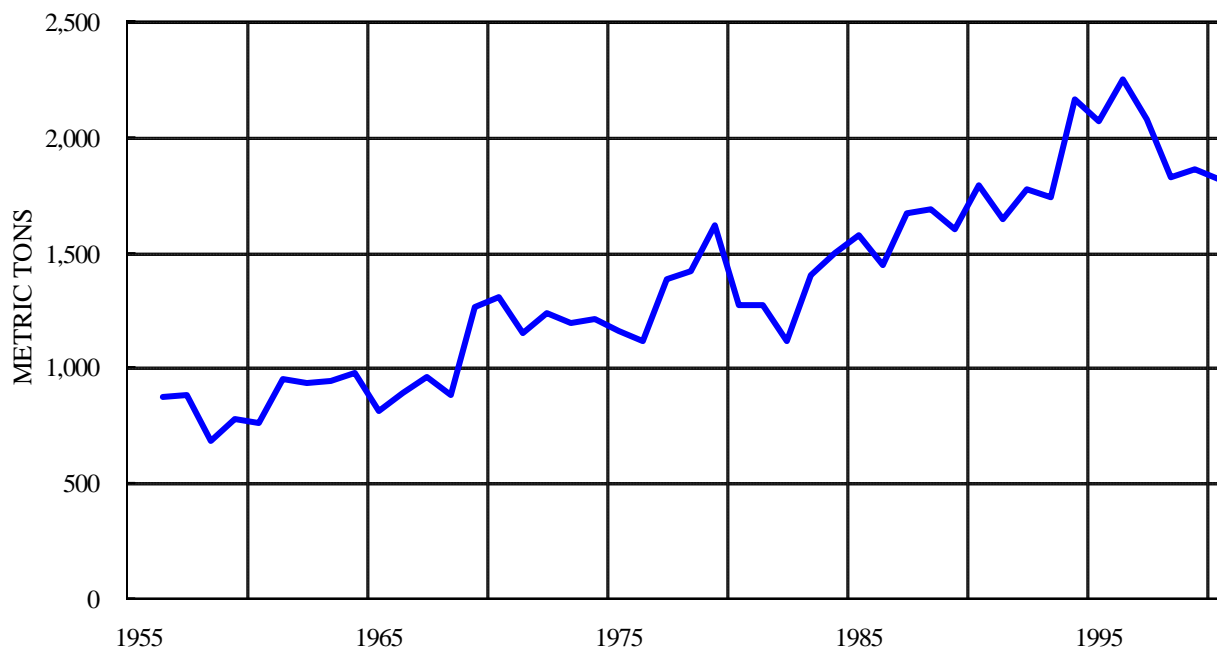


Figure 2. World refinery production of selenium, 1956-2000. [Data from U.S. Bureau of Mines (1940-1994); U.S. Geological Survey (1995-2000)]

U.S. apparent consumption from 1940 through 2000 rose more slowly, at an average rate of only 0.7 percent per year (fig. 3). It peaked at 896 t in 1969 probably owing to demands for military equipment for the Vietnam War. In general, U.S. apparent consumption has been characterized by large year-to-year fluctuations during the entire 60-year period.

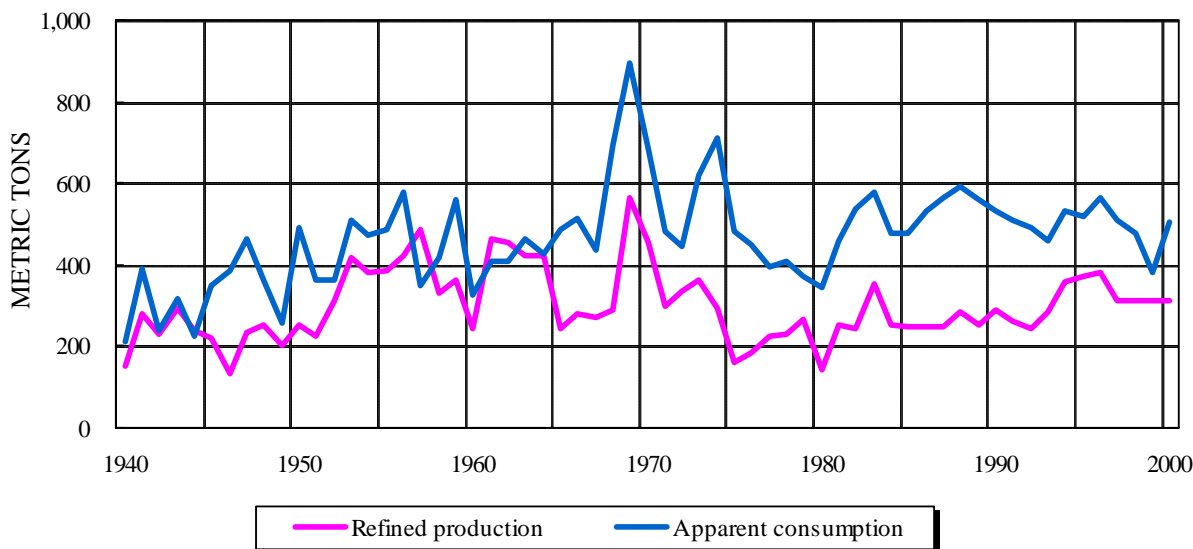


Figure 3. Selenium in the United States, 1940-2000. [U.S. Bureau of Mines (1940–1994); U.S. Geological Survey (1995–2000); refined production for 1997 to 2000 is estimated]

Glass manufacture has been a consistently important market segment for selenium for many years. Since 1965, domestic consumption of selenium in glass manufacture has ranged from about 100 to 175 t/yr; in 2000, at 126 t/yr, it was about 25 percent of total selenium consumption and appears to be stable at that level.

Electronics was the largest use for selenium in the peak consumption years of the 1970s. From 1965 until the 1990s, domestic consumption ranged from about 140 to 230 t/yr, but in the past decade, it has declined steadily as organic photoreceptors have replaced selenium in new copiers, thus leaving only the replacement photoreceptor market for selenium. At 50 t in 2000, it accounted for only 10 percent of total domestic selenium consumption and is expected to decline slowly as older copiers are gradually replaced, thus leaving only the consumption for rectifiers and photocells.

Consumption for chemicals and pigments has ranged from about 60 to 120 t/yr; it was 111 t in 2000, or 22 percent of total domestic selenium consumption. Consumption is split about 65 to 35, chemicals to pigments, or 70 t for chemicals and 40 t for pigments.

With the advent of lead-free plumbing brasses in the past decade, consumption for metallurgical uses has grown to 120 t in 2000, from about 75 t in 1995 or to 24 percent of total domestic consumption from 15 percent. The rate of growth appears to have leveled off somewhat in the past 3 years.

SUBSTITUTES FOR SELENIUM

High-purity silicon has replaced selenium in high-voltage rectifiers and is the major substitute for selenium in low- and medium-voltage rectifiers. Silicon is also a major substitute in solar photovoltaic cells. Amorphous silicon and organic photoreceptors are substitutes in xerographic document copiers. Organic pigments have been developed as substitutes for cadmium sulfoselenide pigments. Other substitutes include cerium oxide as either a colorant or decolorant in glass; tellurium in pigments and rubber compounding; bismuth, lead, and tellurium in free-machining alloys; and bismuth and tellurium in lead-free brasses.

INDUSTRY AND MARKET

Refinery production of selenium is reported by 14 countries. Nearly all the producers are electrolytic copper refineries. Not all copper refineries, however, process their own slimes to recover selenium; some prefer to ship them to the 30 or so refineries that do produce selenium. Secondary selenium is processed at a few of the same refineries that produce primary selenium. In the United States in 2000, only ASARCO Incorporated, Amarillo, Texas, produced commercial-grade selenium; another refiner shipped semirefined selenium to Asia for toll refining. No secondary selenium was processed domestically.

Selenium is traded by 12 companies in the United States and more than 130 worldwide. No count of consumers is available, but most selenium clearly is consumed in the industrialized countries.

The value of selenium consumed in the United States in 2000 is estimated to have been on the order of \$4 million. World production/consumption is estimated to have been on the order of \$15 million.

SELENIUM AND THE ENVIRONMENT

Elemental selenium is relatively nontoxic, as are some of the nearly sixty metallic selenides. However, most selenium compounds, such as the acid-reactive selenides, the oxides, halides, oxyhalides, and organics are highly toxic. Selenium oxyhalides burn and blister skin upon contact. Hydrogen selenide, which is a toxic gas, attacks the mucous membranes of the eyes and upper respiratory tract (Hoffmann and King, 1997, p. 707). Most selenium compounds are believed not to cause cancer. The one compound that has been determined to be a probable carcinogen when ingested is selenium disulfide. The disulfide has not been carcinogenic when placed in contact with skin; its use in antidandruff shampoos is considered to be safe (U.S. Agency for Toxic Substances and Disease Registry, 1997).

Selenium dioxide, which forms when metallic selenium is heated, is the compound of most concern in the workplace; it reacts with perspiration or water to form selenious acid, which is an irritant. It is also the principal selenium species in urban air where most of it is attached to fly ash and aerosol particulates. It forms during the combustion of fossil fuels, which is the source of as much as 90 percent of the selenium in urban air. The selenium level in most urban regions lies in the range from 0.1 to 10 nanograms per cubic meter of air (Spectrum Laboratories, undated).

In the United States, the Environmental Protection Agency has set the maximum level of selenium in drinking water at 50 ppb. The Occupational Safety and Health Administration's exposure limit for selenium compounds in the workplace is 0.2 milligram per cubic meter of air for an 8-hour workday in a 40-hour workweek (U.S. Agency for Toxic Substances and Disease Registry, 1997). Standard procedures for landfilling have not yet been settled (Spectrum Laboratories, undated).

Humans are exposed to selenium in various forms through inhalation, absorption through the skin, and, much more commonly, ingestion with food (where it is associated with proteins). Just as some geographic regions have soils that are deficient in selenium content, other areas, typically characterized by the presence of volcanic rocks, have soils that are rich in selenium. Some of the vegetation in these areas may carry enough selenium to be toxic to animals and humans.

SUPPLY AND DEMAND

SUPPLY AND DISTRIBUTION

Refined selenium was produced in 14 countries in 2000; the four largest producing countries (Belgium, Canada, Japan and the United States) accounted for more than 1,500 t, or an estimated 83 percent of the world total (fig. 4). Although Australia also produced refined selenium, production figures were not available. World refined production has grown at an average rate of about 2.5 percent per year from 1956 (the first year for which data are available for individual countries) through 2000 (fig 2). U.S. refined production over the same period has exhibited large year-to-year fluctuations that have ranged between 150 and 550 t/yr, and has, on average, declined 0.7 percent per year (fig. 3). Production has not kept pace with the growth of domestic copper refining, of which selenium is a

byproduct, but this may be attributed largely to the practice by several domestic refiners of exporting their anode slimes for extraction of precious metals, selenium, and tellurium.

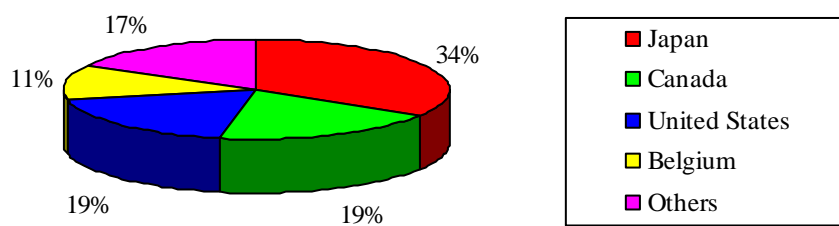


Figure 4. Principal producers of refined selenium, 2000. [U.S. share is estimated. Other data by Brown, 2002]

World consumption figures are not available. U.S. apparent consumption in 2000, however, was equivalent to more than one-fourth of the 1,800-t world refinery output, and Japanese demand was equivalent to nearly one-tenth of world output.

U.S. supply-distribution relationships since 1960 are shown in table 3. From the table and from figure 3, apparent consumption has exceeded supply in nearly every year. The shortfall has been made up by net imports and deliveries from producers' stocks. Secondary selenium has not been recovered domestically for the past two decades, and little was recovered in earlier years. Most end uses are dissipative; the only scrap generated has been worn out or obsolete rectifiers and xerographic photoreceptor drums, and these have routinely been exported for recovery of the selenium.

POTENTIAL SUPPLY

The world selenium reserve base at yearend 2001 was estimated to be about 170,000 t of selenium, and the U.S. reserve base was estimated to be 9,200 t. Both estimates were confined to selenium contained in the deposits that make up the copper reserve bases and further restricted to electrolytically refined primary copper. Leaching/electrowinning technology does not capture byproducts, such as selenium. At the 2001 rates of production and consumption and with a static set of the other market and technological factors operating in 2001, the present world reserve base would last several decades aided by contributions from the recycling of waste and scrap. No attempt will be made, however, to produce numerical estimates of resource lifetimes because the quality of the resource estimates does not warrant it. Moreover, the various market and technological factors that govern production and consumption will likely not remain static.

The U.S. Government has not stockpiled selenium since 1976, and a Government stockpile will not likely be part of the domestic supply in the future.

SUSTAINABILITY OF PRODUCTION AND USE

The production of selenium should easily be sustainable. The resources are adequate and the production process appears to incur no environmental issues that cannot be resolved. The use of selenium appears unlikely to outgrow the supply. Selenium-containing products do not ordinarily pose a threat to human health or the environment; the exception might be cadmium sulfoselenide pigments, but these are being replaced by more-benign rare earth oxide and organic pigments. Toxic selenium chemicals can be used safely in the work place. Thus, the future use of selenium appears likely to be unimpeded.

ECONOMIC FACTORS

The costs of exploration, mining, and metallurgical extraction associated with selenium are grouped with those for the precious metals, tellurium, and other byproduct metals and embedded in the costs of the primary metals, copper and lead. Consequently, they are not readily available.

U.S. selenium prices have been relatively low in recent years; the average price in 1999, \$2.50 per pound, was the lowest annual average in the past half century. The demand for selenium, however, is more influenced by the technological requirements of its end uses and by costs associated with its use as compared with substitute materials than with its initial cost. When selenium prices are low, producers respond by stockpiling anode slimes.

U.S. mine producers are granted a 14-percent depletion allowance on their domestic and foreign production of selenium. The depletion allowance is a business tax deduction analogous to depreciation but is applied to an ore reserve rather than equipment or production facilities. With this deduction, Federal tax law recognizes that an ore deposit is a depletable asset.

Imports into the United States of unwrought selenium metal and selenium dioxide are duty-free.

OUTLOOK

Total selenium consumption in the United States is likely to remain in the range of from 400 to 550 t/yr during the next few years; this will be the result of a combination of stable and countervailing trends among the end uses. Consumption in the glass/ceramics and chemicals/pigments categories has been stable for many years and will probably continue to be so, although the pigments sector could shrink a little. Consumption in the electronics category will continue to trend downward as the older selenium-using xerographic copiers are retired, whereas the metallurgical use of selenium, especially in lead-free plumbing brasses and in steels, should continue to grow.

The present reserve base of selenium in the United States and the world is adequate for at least three to four decades, assuming growth rates for consumption that are in line with past trends.

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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).