5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

Selenium is distributed widely in nature and is found in most rocks and soils at concentrations between 0.1 and 2.0 ppm (Fishbein 1983). However, elemental selenium is seldom found naturally, but it is obtained primarily as a byproduct of copper refining (Fishbein 1983). Selenium is contained in the constituents of the copper anode that are not solubilized during the copper refining process and ultimately accumulate on the bottom of the electrorefining tank. These constituents, usually referred to as slimes, contain roughly 5–25% selenium and 2–10% tellurium. Selenium is commercially produced by either soda ash roasting or sulfuric acid roasting of the copper slimes.

Soda Ash Roasting. A soda ash binder is mixed with the slimes and water to form a stiff paste. The paste is extruded or pelletized and allowed to dry and then roasted at 530–650 °C. The roasted product is then ground and leached into water. The resultant hexavalent selenium dissolves as sodium selenate, Na_2SeO_4. The sodium selenate may be reduced by controlled heating to sodium selenide, which is leached with water to form a liver-red solution of sodium selenide that is readily oxidized to the elemental form by blowing air through the solution (Hoffmann and King 1997). A second process for the reduction of hexavalent selenium involves the use of concentrated hydrochloric acid or ferrous iron salts catalyzed by chloride ions as the reductant (Hoffmann and King 1997).

Sulfuric Acid Roasting. In this method, the copper slimes are mixed with sulfuric acid and roasted at 500–600 °C to produce selenium dioxide, which volatilizes readily at the roasting temperature. The selenium dioxide is reduced to elemental selenium during the scrubbing process with sulfur dioxide and water. The resultant commercial-grade selenium can be purified to 99.5–99.7% (Hoffmann and King 1997).

The U.S. production of selenium was 373 and 379 metric tons in 1995 and 1996, respectively (USGS 2001, 2002). No production data were reported for the years 1997–2001. All of the primary selenium producers in the United States are electrolytic copper refiners. Asarco Incorporated and Kennecott Utah Copper Corporation produce refined selenium in the United States (Hoffmann and King 1997; SRI 2000). Two other copper refiners, Phelps Dodge Corporation and Magma Copper Company, send selenium or

selenium-bearing copper slimes outside of the United States for final processing (Hoffmann and King 1997).

Tables 5-1 and 5-2 list facilities in each state that produce, process, or import selenium and selenium compounds, respectively, for commercial use. The data do not include facilities such as electric power generating plants that release selenium unintentionally as a by-product. The intended use and the range of maximum amounts of these substances that are stored on site are also included. The data listed in these tables are derived from the Toxics Release Inventory (TRI00 2002). Only certain types of facilities were required to report. Therefore, this is not an exhaustive list.

5.2 IMPORT/EXPORT

The import volumes of selenium were 324, 428, 346, 339, 326, 452, and 500 metric tons for 1995, 1996, 1997, 1998, 1999, 2000, and 2001, respectively (USGS 2001, 2002). The U.S. exports of selenium were 270, 322, 127, 151, 233, 89, and 75 metric tons for 1995, 1996, 1997, 1998, 1999, 2000, and 2001, respectively (USGS 2001, 2002).

5.3 USE

In electronics, selenium's semiconductor and photoelectric properties make it useful in "electric eyes," photographic exposure meters, and rectifiers for home entertainment equipment. In addition, a large proportion of the available selenium is used to coat the metal cylinders from which a photographic image is transferred in xerography (Fishbein 1983). Selenium is widely used in the glass industry to counter coloration that results from iron impurities. It is also used in the production of both red and black glasses (Fishbein 1983). Selenium is contained in pigments that are used in plastics, paints, enamels, inks, and rubber (Fishbein 1983). Selenium is used as a catalyst in the preparation of pharmaceuticals including niacin and cortisone, as an ingredient in antidandruff shampoos (selenium sulfide), and as a constituent of fungicides (selenium sulfide) (IARC 1975a). Radioactive selenium is used in diagnostic medicine and aids in the visualization of difficult-to-study malignant tumors (Fishbein 1983; Jereb et al. 1975). Selenium is contained in some dietary supplements at concentrations in the range of 10–25 µg/tablet (Goodman et al. 1990). Selenium is also used as a nutritional feed additive for poultry and livestock, in pesticide formulations, and as an accelerator and vulcanizing agent in rubber production (Fishbein 1983; NAS 1976a). Table 5-3 lists some specific uses of selected selenium compounds.

Table 5-1. Facilities that Produce, Process, or Use Selenium

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AZ	1	1,000	9,999	12
CA	2	100	99,999	12
IA	1	100	999	7
IL	1	1,000	9,999	7
IN	2	100,000	999,999	8
LA	1	1,000	9,999	12
MI	1	0	99	12
OK	1	100	999	1, 5
OR	1	100,000	999,999	12
PA	2	10,000	99,999	6, 8
SC	1	10,000	99,999	1, 3, 4, 5, 9, 12, 13
WA	1	100	999	14
WY	1	0	99	1, 13

Source: TRI00 2002

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

Table 5-2. Facilities that Produce, Process, or Use Selenium Compounds

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	4	100	99,999	1, 3, 4, 5, 8, 9, 12, 13
AR	1	10,000	99,999	12
AZ	2	10,000	999,999	1, 3, 4, 5, 9, 13, 14
CA	1	10,000	99,999	8, 9
FL	1	1,000	9,999	1, 5, 9, 12, 13, 14
GA	5	1,000	99,999	1, 2, 3, 4, 5, 6, 9, 13
IA	2	100	9,999	3, 4, 7, 8
ID	1	100,000	999,999	1, 5
IL	3	1,000	99,999	1, 5, 7, 12, 13
IN	4	0	99,999	1, 5, 7, 9, 12, 13
KY	5	100	99,999	1, 3, 4, 5, 9, 12, 13
LA	1	10,000	99,999	1, 3, 4, 5, 6, 8
MA	1	10,000	99,999	1, 5
MD	2	1,000	99,999	1, 3, 4, 5, 6, 13
MI	4	1,000	999,999	1, 2, 3, 4, 5, 8, 9, 12, 13
MN	1	1,000	9,999	1, 2, 9, 13, 14
MO	1	10,000	99,999	7
MT	1	10,000	99,999	1, 5, 12, 14
NC	3	10,000	99,999	1, 3, 4, 5, 9, 12, 13, 14
NM	4	0	99,999	1, 3, 4, 5, 9, 12, 13
NV	6	10,000	9,999,999	1, 5, 6, 10, 13, 14
OH	8	1,000	9,999,999	1, 3, 4, 5, 7, 9, 12, 13, 14
OK	1	1,000	9,999	8
PA	8	0	999,999	1, 4, 5, 6, 9, 12, 13, 14
SC	1	10,000	99,999	1, 3, 4, 5, 9, 12, 13
TN	2	1,000	99,999	1, 5
TX	10	10,000	999,999	1, 2, 3, 4, 5, 6, 8, 9, 12, 14
UT	4	10,000	9,999,999	1, 3, 4, 5, 6, 9, 12, 13
VA	1	10,000	99,999	1, 5
WV	9	100	99,999	1, 3, 4, 5, 9, 12, 13, 14
WY	2	0	99,999	1, 4, 5, 9, 12, 13

Source: TRI00 2002

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

Table 5-3. Some Selenium Compounds and Their Uses[a]

Compound	Use
Elemental selenium	In rectifiers, photoelectric cells, blasting caps, xerography, stainless steel; as a dehydrogenation-catalyst
Sodium selenate (Na_2SeO_4)	As an insecticide; in glass manufacture; in medicinals to control animal diseases
Sodium selenite (Na_2SeO_3)	In glass manufacture; as a soil additive for selenium-deficient areas
Selenium diethyldithio-carbamate	Fungicide; vulcanizing agent
Selenium disulfide (SeS_2)	In veterinary medicine
Selenium sulfide (SeS)	In anti-dandruff shampoos and in veterinary medicine
Selenium dioxide (SeO_2)	Catalyst for oxidation, hydrogenation, or dehydrogenation of organic compounds
Selenium hexafluoride (SeF_6)	As a gaseous electric insulator
Selenium oxychloride ($SeOCl_2$)	Solvent for sulfur, selenium, tellurium, rubber, bakelite, gums, resins, glue, asphalt, and other materials
Aluminum selenide (Al_2Se_3)	Preparation of hydrogen selenide for semi-conductors
Ammonium selenite [$(NH_4)_2SeO_3$]	Manufacture of red glass
Cadmium selenide	Photoconductors, photoelectric cells, rectifiers
Cupric selenate ($CuSeO_4$)	In coloring copper and copper alloys
Tungsten diselenide (WSe_2)	In lubricants

[a]Adapted from Fishbein 1983

The 2002 consumption patterns for selenium by industry were as follows: glass manufacturing, 35%; chemicals and pigments, 20%; electronics, 12%; and miscellaneous (including agriculture and metallurgy), 33% (USGS 2002).

5.4 DISPOSAL

Selenium was listed by EPA in 1973 as a nonradioactive hazardous element and, as such, is subject to many regulations (Dawson and Mercer 1986). Selenium compounds should be stored in a dry area to avoid contamination of water with selenium and to decrease the hazards that may result from human exposure to selenium-contaminated water (ITII 1976).

Disposal and waste treatment consist of treating an acidified solution of selenium with sodium sulfite to form the reducing agent sulfur dioxide. The selenium solution is then heated to produce elemental selenium, which is less mobile in the environment and less bioavailable, and the solution is filtered and washed (ITII 1976).

According to the TRI, in 2000, an estimated 76,248 pounds of elemental selenium and 1,782,654 pounds of selenium compounds were transferred off-site, presumably for disposal (TRI00 2002).