

US EPA ARCHIVE DOCUMENT

SELENIUM

A. Commodity Summary

Selenium is found in 75 different mineral species, however, pure selenium does not exist as an ore. For this reason, primary selenium is recovered from anode slimes generated in the electrolytic refining of copper. One facility, ASARCO - Amarillo, TX, processes this slime further to recover tellurium. For more information on tellurium recovery, see the tellurium report. According to the U.S. Bureau of Mines, three copper refineries, Asarco, Phelps Dodge, and Kennecott, accounted for all of the domestic production of primary selenium. The 1994 production was worth \$3 million. End uses of selenium include:

- electronics, 35%;
- chemicals and pigments, 20%;
- glass manufacturing, 30%; and
- other, including agriculture and metallurgy, 15%. ¹

Exhibit 1 lists the names and locations of the facilities involved in the production of selenium.

EXHIBIT 1

SUMMARY OF SELENIUM PROCESSING FACILITIES

Facility Name	Location
ASARCO	Amarillo, TX
Kennecott (RTZ)	Garfield, UT
Phelps Dodge	El Paso, TX

B. Generalized Process Description

1. Discussion of Typical Production Processes

Generally, 30-80% of the selenium contained in copper anode slimes is recovered by commercial operations. Several methods of selenium recovery may be used. The two major processes for selenium recovery are smelting with soda ash and roasting with soda ash. Exhibits 2 through 4 present process flow diagrams for selenium production. Other methods include roasting with fluxes, during which the selenium is either volatilized as an oxide and recovered from the flue gas, or is incorporated in a soluble calcine that is subsequently leached for selenium. In some processes, the selenium is recovered both from the flue gas and from the calcine. At the process end points, selenium metal is precipitated from solutions of sodium selenite or selenious acid by sulfur dioxide.²

¹ Stephen Jasinske, "Selenium," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 150-151.

² Neldon Jenson, "Selenium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp. 705-711.

EXHIBIT 2
SODA ROASTING

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-187--193.

EXHIBIT 3
SODA SMELTING

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-187--193.

EXHIBIT 4
SELENIUM PURIFICATION

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-187--193.

2. Generalized Process Flow

Roasting with Soda Ash

As shown in Exhibit 2, decopperized slime is roasted with soda ash to produce sodium selenite and sodium selenate. The selenium is then leached with water, neutralized to precipitate tellurium, and then sparged with SO_2 to precipitate selenium.³

Smelting with Soda Ash

As shown in Exhibit 3, decopperized slime is mixed with soda ash and silica and smelted in a furnace. Slag containing silica, iron, and several other metal impurities is generated as waste. The molten charge containing selenium is aerated to oxidize and volatilize the selenium, and the remaining solids are removed for precious metal recovery. The soda ash is leached with water and filtered to separate unwanted solid impurities, which are discarded as waste. The selenium-containing filtrate is neutralized to precipitate out tellurium, and is acidified to precipitate selenium. The selenium containing sludge is then boiled, washed, dried, and a pulverized to yield the selenium product.⁴

Selenium Purification

The selenium obtained from either smelting with soda ash or roasting with soda ash is then purified. As shown in Exhibit 4, the crude selenium is dissolved in sodium sulfite, and the resulting solution is filtered to remove unwanted solids as waste filter cake. The resulting filtrate is acidified with sulfuric acid to precipitate the selenium. The selenium precipitate is distilled to drive off impurities, producing a high purity selenium for commercial and industrial use.

Kennecott Copper Corp.

Kennecott Copper Corp., recovers selenium from anode slimes at its Garfield facility through fusion with sodium bisulfate to oxidize copper-silver selenide compounds and other slime constituents. Both SO_2 and SeO_2 are evolved during the fusion, and are absorbed in water in the gas scrubbing and Cottrell system as H_2SeO_3 and H_2SO_3 . The H_2SeO_3 slowly oxidizes the H_2SO_3 to H_2SO_4 and red amorphous selenium is precipitated. Periodically, elemental selenium is harvested from the settling tanks and other parts of the scrubber and Cottrell circuit. The red amorphous selenium, harvested from the scrubber system, is coked with hot water and steam to convert it to a gray crystalline form. Coked selenium is used for preparation of commercial grade selenium without further purification. Commercial selenium is produced by drying coked selenium, grinding, and sizing by screening. The material is packaged and sold.⁵

High purity selenium is currently produced from crude coked selenium. After wet grinding, pulping, and decantation washing with hot water to (remove impurities such as arsenic), the high purity circuit feed is leached with hot sodium sulfite solution. Selenium dissolves to form a compound similar to sodium thiosulfate. After leaching, the slurry settles and the solution is decanted through a clarifier press to the precipitation tanks. Selenium is precipitated by acidification of this solution with concentrated H_2SO_4 . The solutions are kept cool during acidification to obtain red amorphous selenium. After precipitation, the slurry is settled and most of the solution decanted to waste. Settled slurry is repulped with water and heated with steam. Heating converts the red selenium to a gray crystalline powder. The slurry is then centrifuged in a perforated bowl centrifuge and the solids washed by displacement with copious amounts of water.

Centrifuge cake is charged into the first stage of the three stage distillation circuit. Condensed selenium from these stills is collected in fractionating trays. Samples for spectrographic analysis of 19 elements are taken through the run. Early fractions are high in tellurium and other high-boiling-point impurities. Impure fractions are rejected to sulfite leaching or redistillation in the first-stage stills. Acceptable fractions from the first-stage stills are advanced to second-stage distillation in a silicon carbide retort. Condensed selenium from this stage is passed through a shotter (pelletizer) and quenched with water. Seven fractions are normally made and a sample of each is analyzed spectrographically for 19 impurity elements. First and last fractions, as well as others showing abnormal impurity levels, are recycled to an appropriate part of the purification circuit. Acceptable fractions are advanced to third-stage distillation. Condensed selenium shot from third-stage distillation is again collected in seven fractions, each of which is analyzed spectrographically. Reject fractions are recycled back to an appropriate part of the circuit. Acceptable selenium shot

³ Ibid.

⁴ U.S. Environmental Protection Agency, "Selenium," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-187--193.

⁵ Arnold M. Lansche, "Selenium and Tellurium - A Materials Survey," U.S. Bureau of Mines. Information Circular 8340, 1967, pp. 32-34.

from third-stage distillation is made up into lots and blended. Samples from the blended material are analyzed again spectrographically and chemical analysis is made for halogens, sodium sulfur, and nonvolatile material. Finally, acceptable lots are packaged for sale or stored for doped selenium production.⁶

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

None identified.

4. Beneficiation/Processing Boundaries

Since selenium is recovered as a by-product of other metals, all of the wastes generated during selenium recovery are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, see the report for copper presented elsewhere in this document.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Not applicable.

2. Mineral Processing Wastes

Selenium is recovered from anode slimes generated from the electrolytic refining of copper. Because of this, all wastes from selenium production generated after the production of the copper anode slimes are mineral processing wastes. Listed below are possible waste streams from selenium production.

Plant process wastewater (PWW). This waste may exhibit the characteristic of toxicity for lead. In addition, this waste may also exhibit the characteristic of corrosivity since it is expected to have a pH of 0.8 to 1.9. The 1991 generation rate for the sector was 66,000 metric tons per year.⁷ Waste characterization data are presented in Attachment 1. This waste may be recycled and is classified as a spent material.

Slag. This waste may contain silica, iron, and other metal impurities. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 50 metric tons/yr, 500 metric tons/yr, and 5000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for selenium. Slag may be recycled and is classified as a byproduct.

Spent filter cake. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 50 metric tons/yr, 500 metric tons/yr, and 5,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for selenium. This waste may be recycled and is classified as a byproduct.

Tellurium slime waste are sent to tellurium product recovery. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 50 metric tons/yr, 500 metric tons/yr, and 5,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for selenium. This waste is classified as a byproduct.

Waste solids. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 50 metric tons/yr, 500 metric tons/yr, and 5,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for selenium.

⁶ Ibid.

⁷ U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, Vol. I, August, 1992, pp. I-2 - I-8.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naphtha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, waste oil (which may or may not be hazardous), and other lubricants.

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