

US EPA ARCHIVE DOCUMENT

TELLURIUM

A. Commodity Summary

According to the U.S. Bureau of Mines, commercial grade tellurium and tellurium dioxide are recovered from anode slimes at one electrolytic copper refinery in the United States (ASARCO - Amarillo, TX). Selenium is also recovered from the copper anode slimes during this process (see Selenium). High purity tellurium, tellurium master alloys, and tellurium compounds are produced by primary and intermediate processors from commercial-grade metal and tellurium dioxide. Tellurium is used mainly in the production of free-machining steels. It is also used as a minor additive in copper and lead alloys and malleable cast iron, as an accelerator in rubber compounding, in thermoelectric applications, and as a semiconductor in thermal-imaging and photoelectric applications. Tellurium is added to selenium-base photoreceptor alloys to increase the photo speed. In 1994, iron and steel products remained the largest end use, followed by nonferrous metals, chemicals, and other uses.¹ Some common commercial tellurium products include tellurium dioxide, sodium tellurate, ferrotellurium, and tellurium diethyldithiocarbamate.²

B. Generalized Process Description

1. Discussion of Typical Production Processes

Nearly all tellurium is obtained as a byproduct of the electrolytic refining of copper. Although copper slimes are valued primarily for gold, silver, and occasionally platinum-group metals, tellurium is available to the refiner for the added cost of recovery and refining.³ Tellurium is present in copper refinery slimes in concentrations ranging from a trace to 8 percent and is recovered as precipitated tellurous acid. Tellurium metal can be produced from the crude tellurous acid by one of three purification methods described below. Metal tellurides for semiconductors are made by direct melting, after which, the excess tellurium is volatilized under reduced pressure. The resultant tellurium vapor is then passed over a heated metal in an inert gas carrier and undergoes a high temperature reduction of oxy compounds with hydrogen or ammonia.⁴

2. Generalized Process Flow Diagram

The process flow for the production of tellurium can be separated into two stages. The first stage involves the removal of copper from the copper slimes (an intermediary product is tellurous acid). The second stage involves the recovery of tellurium metal and purification of the recovered tellurium. The process flow diagrams for a typical recovery process are presented in Exhibits 1 through 3. Exhibit 1 shows the steps involved in producing tellurous acid from copper anode slimes. The process flow diagrams for two methods of recovering tellurium metal from tellurous acid, acid precipitation and electrolytic purification, are presented in Exhibits 2 and 3, respectively.

¹ Stephen M. Jasinski, "Tellurium," from Mineral Commodities Summary, U.S. Bureau of Mines, 1995, pp. 172-173.

² "Tellurium," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXII, 1983, p. 663.

³ Neldon L. Jensen, "Tellurium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, p. 825.

⁴ "Tellurium," 1983, Op. Cit., p. 663.

EXHIBIT 1

TELLURIUM RECOVERY FROM COPPER SLIMES

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 204-210.

Removal of copper and production of tellurous acid

Since tellurium is recovered from copper refinery slimes, the first step in the recovery process shown in Exhibit 1 is the removal of copper from the slimes. Copper is generally removed by aeration in dilute sulfuric acid, oxidative pressure-leaching with dilute sulfuric acid, or digestion with strong acid followed by water-leaching. During the copper removal, much of the tellurium is dissolved. This tellurium is recovered by cementing (precipitation of metallic copper), leaching the cement mud with dilute caustic soda, and neutralizing with sulfuric acid. The precipitate from the neutralization contains tellurium as tellurous acid suitable for recovery.⁵ Some of the liquid wastes from this neutralization/precipitation step are sent to selenium recovery.

Copper-free slimes are treated by one of the four following methods: (1) refining with soda ash in a dore or cupeling furnace; (2) combined oxidation and alkalization by roasting or baking a slime-soda ash mix; (3) removal of selenium by roasting and caustic soda leaching; or (4) boiling the slime with caustic soda. The soda slag from the soda refinement or the roasted product of the oxidation is leached with water to extract sodium tellurite. The insoluble sodium tellurate in the leached slag is returned to the copper-anode furnace. The liquor obtained from the selenium removal and the boiling with caustic soda contains lead. In all cases, the solution contains selenium and impurities. Whatever the method, the liquor is neutralized to pH 6-6.2 with sulfuric acid to precipitate impure tellurous acid as tellurium mud, which contains lead sulfate, silica, and other impurities. The mud is purified by redissolving in caustic soda and reprecipitating. Impurities, such as lead are, removed by careful precipitation from the caustic solution with sodium sulfide. Fractional neutralization of the initial impure caustic solution yields tellurous acid of a purity acceptable for reduction to the metal.⁶

Recovery and purification of tellurium

Tellurium is recovered from the precipitated tellurous acid by three methods: (1) direct reduction; (2) acid precipitation; and (3) electrolytic purification. The electrolytic purification method is the preferred method.⁷ The high boiling temperature of tellurium precludes purification by atmospheric distillation, but low pressure distillation is feasible. Heavy metal impurities (iron, copper, tin, lead, antimony, bismuth) remain in the still residue. Volatile selenium is a persistent contaminant, and may be as high as 500 ppm in the distilled tellurium.⁸

Direct Reduction. Some of the drawbacks associated with direct reduction include heavy fuming of telluride dioxide and the formation of organic decomposition products. The reduction with sulfur is rapid and leaves a clean melt, but the heavy fumes are problematic.⁹

Acid Precipitation. As presented in Exhibit 2, purification by acid precipitation first involves dissolving the crude tellurous acid solids in hydrochloric acid or sulfuric acid. Crude common salt is added to the acidified solution, and tellurium is precipitated by adding sulfur dioxide. The resultant precipitate undergoes filtration, washing, drying, and melting. In an alternative method, tellurium is dissolved in

⁵ Ibid., p. 662.

⁶ Ibid.

⁷ Ibid.

⁸ Ibid.

⁹ Ibid.

EXHIBIT 2

PURIFICATION OF TELLURIUM BY ACID PRECIPITATION

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 204-210.

EXHIBIT 3
ELECTROLYTIC PURIFICATION OF TELLURIUM

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 204-210.

a strong nitric acid, hydrolyzed to white $2\text{TeO}_2\cdot\text{NO}_3$ and precipitated by diluting and boiling, and separating. The resultant precipitate is washed (redissolving and rehydrolyzing, if desired), dissolved in hydrochloric acid, and reduced with sulfur dioxide. Ultra high-purity tellurium is prepared by zone refining in a hydrogen or inert-gas atmosphere.¹⁰

Electrolytic Purification. As shown in Exhibit 3, electrolytic purification involves dissolving crude tellurous acid solids in caustic soda to yield a solution containing sodium tellurite and free caustic soda. The solution then undergoes electrolysis in a cell equipped with stainless-steel electrodes. The cathodes are then removed, washed, dried, and melted.¹¹

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

None Identified.

4. Beneficiation/Processing Boundary

Since tellurium is recovered from anode slimes from a copper refinery, all wastes generated by this mineral commodity sector are mineral processing wastes. For a description of the beneficiation/processing boundary for this sector, please see the report on copper presented elsewhere in this background document.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Not Applicable

2. Mineral Processing Wastes

Recovery from Copper Anode Slimes

Slag. As shown in Exhibit 1, slag is generated from roasting and leaching. Slag from leaching may be wasted or returned to a copper anode for further processing while the slag from roasting is wasted.¹² 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 100 metric tons/yr, 1,000 metric tons/yr, and 4,500 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of toxicity for selenium. This waste is classified as a by-product.

Solid waste residues. Solids, likely containing sulfur, are generated from precipitation as impurities and are discarded as waste.¹³ 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 100 metric tons/yr, 1,000 metric tons/yr, and 4,500 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for selenium.

Wastewater. There is wastewater associated with the neutralization steps that follow both the addition of sulfuric acid and the addition of sodium sulfide in Exhibit 1. The liquid resulting from the addition of sulfuric acid is sent to selenium recovery. Generation rate estimates for this waste stream are included in the estimates for the wastewater stream from purification of tellurous acid as discussed below.

Purification of Tellurous Acid

The following wastes have been identified as generated during the purification step.

¹⁰ Ibid.

¹¹ Ibid.

¹² U.S. Environmental Protection Agency, "Tellurium", from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, Office of Solid Waste, 1988, pp. 204 - 210.

¹³ U.S. Environmental Protection Agency, 1988, Op. Cit., pp. 204 - 210.

Fumes of Telluride dioxide. Telluride dioxide fumes are generated during the direct reduction step.

Wastewater. One of the waste streams associated with the acid precipitation step of tellurium recovery is wastewater from washing, with an acidic pH. 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 100 metric tons/yr, 10,000 metric tons/yr, and 20,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristics of toxicity (selenium) and corrosivity. This waste is classified as a spent material.

Waste Electrolyte. Waste electrolytes are generated during electrolytic purification. 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 100 metric tons/yr, 1,000 metric tons/yr, and 10,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (lead and selenium).

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.

BIBLIOGRAPHY

Jasinski, Stephen M. "Tellurium." From Mineral Commodities Summary. U.S. Bureau of Mines. 1995. pp. 172-173.

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