

US EPA ARCHIVE DOCUMENT

TIN

A. Commodity Summary

The primary source of tin is the mineral cassiterite, SnO₂, which occurs in vein and lode deposits. More than 80% of the tin ore in the world is found in placer deposits with tin content as low as 0.015%.¹ Final uses of tin include cans and containers, electrical components, construction, transportation, and other uses.²

China and Brazil are the world's largest producers of tin, followed by Indonesia and Bolivia. These countries account for 77% of U.S. tin imports. Tin production in the United States is negligible, with small amounts of tin concentrates mined from a placer deposit at Cache Creek Gold Mine near Fairbanks, Alaska in 1993.³ The sole U.S. tin smelter in Texas City, Texas ceased production in 1989.⁴

B. Generalized Process Description

1. Discussion of Typical Production Processes

Tin concentrate is processed by smelting and refining. Prior to smelting, any impurities in the concentrate are removed by roasting, leaching with water, and acid leaching. Cassiterite, a carbon reducing agent, and limestone and silica are smelted to create molten tin, which is cast in slabs. These slabs are then refined either pyrometallurgically or electrolytically.

2. Generalized Process Flow Diagram

Tin smelting is most commonly conducted in reverberatory furnaces because they offer better process control and yield cleaner slags. Electric furnaces are sometimes used by smaller smelters for their energy efficiency.⁵ Blast furnaces, kilns, and horizontal furnaces are used to smelt low-grade tin concentrate.⁶

As shown in Exhibit 1, smelting is conducted as a batch operation in which a charge of cassiterite (tin oxide) concentrate, a carbon reducing agent (coke), and fluxes consisting of limestone and silica is smelted for 10 to 12 hours in a two-stage process. In the first stage, carbon monoxide is formed in the furnace and reacts with cassiterite (tin oxide concentrate) to produce tin and carbon dioxide. The silica flux reacts with cassiterite under reducing conditions to yield stannous silicate. Iron, which is also present in the concentrate, reacts with silica to yield ferrous silicate. In the second stage, the silicates fuse with

¹ "Tin and Tin Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXIII, 1983, pp. 18, 23.

² J. Carlin, "Tin," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 182-178.

³ Randol Mining Directory 1994/95, p. 189.

⁴ J. Carlin, 1994, Op. Cit., pp. 182-183.

⁵ U.S. Bureau of Mines, Mineral Facts and Problems, Bulletin 675, 1985, p. 850.

⁶ Carr, D., ed., Industrial Minerals and Rocks, Society for Mining, Metallurgy, and Exploration, Inc., 1994, p. 672.

EXHIBIT 1
TIN SMELTING PROCESS

Graphic Not Available.

Source: U.S. Environmental Protection Agency, "Tin," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-214.

fluxes to create a liquid slag. Unreacted carbon in the fuel reduces the stannous silicate to tin and the ferrous silicate to iron.^{7,8} In addition to molten tin and slag, an off-gas is also generated and is sent to a caustic scrubber to control sulfur dioxide emissions. Additional wastes include brick linings from the furnace and spent fabric filters, both of which are recycled.

After smelting, the batch is tapped into a settler; slag overflows the settler and is collected and resmelted, while the remaining molten tin is cast into slabs (tin anodes) to be refined.⁹ Crude tin is most commonly refined by heat treatment (pyrometallurgical) but can also be refined by electrolytic methods.

Heat treatment consists of heating the tin slab slightly above its melting point but below the melting points of impurities, such as iron and copper. The molten tin is poured into kettles and agitated in a process called boiling. Remaining impurities collect in a surface layer of dross, which is skimmed and resmelted. The remaining tin, with a purity greater than 99.8%, is cast in molds.

Electrolytic refining (see Exhibit 1) requires greater capital expenditures for equipment but yields a purer product. Electrorefining may be conducted in either an acid or alkaline bath.¹⁰ The acid bath consists of stannous sulfate, creosulfonic or phenolsulfonic acids, and free sulfuric acid with beta naphthol and glue to prevent deposits from forming on the cathodes. Slimes can form on the tin anodes if the anodes have high lead levels; the slimes are scrubbed off. The alkaline bath consists of potassium or sodium stannite and free alkali. Lead is precipitated as lead plumbite in slimes that form on the anodes. Pure tin generated in either bath is recast into ingots for sale.¹¹ Waste slimes and waste acid or alkaline baths are shipped off-site for reprocessing and recycle.

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

A research program is being conducted at the Colorado School of Mines for developing a pyrochemical process using molten salts for recovering reactive metals, including tin, from beneficiated ore. The process takes place in a hybrid reactor combining electrolytic production of a calcium reductant and *in situ* utilization of the reductant to reduce metal compounds, specifically tin oxide. The reactor operates at a temperature less than 1,000°C. The technology is reported to generate little waste.¹²

4. Beneficiation/Processing Boundary

EPA established the criteria for determining which wastes arising from the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming

⁷ U.S. Environmental Protection Agency, "Tin," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-214.

⁸ Carr, D., ed., 1994, Op. Cit., p. 672.

⁹ U.S. Bureau of Mines, 1985, Op. Cit., p. 850.

¹⁰ "Tin and Tin Alloys," 1983, Op. Cit., p. 23.

¹¹ U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-214.

¹² Mishra, B., D. Olson, and W. Averill, "Applications of Molten Salts in Reactive Metals Processing," presented at the Conference for Emerging Separation Technologies for Metals and Fuels, Palm Coast, FL, March 13-18, 1993, sponsored by the Minerals, Metals, & Materials Society, Warrendale, PA.

ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in this section.

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between acid leaching and smelting. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where a significant chemical change to the cassiterite occurs. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Waste streams include tailings slurry and process waste water from mining placer deposits, which are held in a tailings pond for settling of solids. The remaining water is either discharged to receiving waters through an NPDES outfall or reused in the mining process.¹³ Most likely contaminants are arsenic, lead, and zinc. Other beneficiation wastes generated during roasting and acid leaching include spent waste acids, sludges, and waste liquids.

2. Mineral Processing Wastes

Smelting operations generate solid, liquid, and gaseous wastes. However, since tin is no longer produced domestically, these waste streams were not included in our analysis.

Slag

Slag is generated during smelting of tin concentrates through the fusion of ferrous silicate with limestone flux. Slag is collected when molten tin is tapped into a settler. Slag is believed to be resmelted and is therefore most likely not disposed as a solid waste. The Newly Identified Mineral Processing Waste Characterization Data Set (NIMPW Characterization Data Set) indicates that, when operating, the sole U.S. tin smelter generated approximately 15,000 metric tons of slag annually.¹⁴ Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Process Wastewater and Treatment Impoundment Sludge

Process wastewater is generated as blowdown from the scrubbing of off-gases generated during smelting. Approximately 83,000 metric tons are generated annually by two plants when they are operating;¹⁵ in 1984, the Texas City smelter generated 22,000 liters of wastewater per metric ton of tin produced.¹⁶ Process wastewater is disposed in impoundments and treated by chemical precipitation and sedimentation; solids settle to create treatment impoundment sludge.

¹³ U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-211.

¹⁴ U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, August 1992, p. I-7.

¹⁵ Ibid.

¹⁶ U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-214.

EP toxicity tests conducted in 1984 on samples of scrubber solids and pond water revealed the wastes to exhibit the characteristic of EP toxicity for arsenic (15.5 ppm for scrubber solids, 22.9 ppm for scrubber pond water).¹⁷ Sampling results are shown in Attachment 1.

Brick Lining and Fabric Filters

Furnaces used in smelting tin concentrates are lined with brick, which periodically must be replaced. Spent brick is resmelted for its tin value.

Fabric filters used in baghouses for filtering off-gases are recycled when spent.

Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Refining, both through heat treatment (pyrometallurgically) and electrolytically, generate solid and liquid wastes, as described below.

Dross

Dross forms during pyrometallurgical refining when tin slab is heated above its melting point; impurities such as lead and copper are captured in a layer of dross at the surface of the molten tin. Dross is skimmed and resmelted. 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 0 metric tons/yr, 100 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (lead).

Waste Acid and Alkaline Baths

A waste electrolyte stream (waste baths), generated in electrolytic refining, most likely contains high metals concentrations and may exhibit the corrosivity and EP toxicity characteristics.¹⁸ Waste baths are shipped off-site for reprocessing.¹⁹ 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 0 metric tons/yr, 100 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (arsenic, cadmium, chromium, lead, and mercury) and corrosivity.

Slimes

Slimes, which form on tin anodes during electrolytic refining, may be corrosive and contain high levels of lead. Slimes are shipped off-site for reprocessing.²⁰ 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 0 metric tons/yr, 100 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (lead) and corrosivity.

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, and waste oil and other lubricants.

¹⁷ U.S. Environmental Protection Agency, 1992, *Op. Cit.*, pp. 34-2.

¹⁸ U.S. Environmental Protection Agency, 1988, *Op. Cit.*, p. 3-212.

¹⁹ U.S. Environmental Protection Agency, 1988, *Op. Cit.*, p. 3-215.

²⁰ *Ibid.*

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