

BISMUTH

A. Commodity Summary

According to the Bureau of Mines, bismuth is produced, as a byproduct of lead refining, at only one facility (ASARCO - Omaha, NE). Reported consumption of bismuth was estimated at 1,500 metric tons during 1994 and 40 companies in the East were responsible for 98 percent of the total bismuth consumption. Bismuth is used primarily in the following industries: pharmaceuticals and chemicals (including cosmetics), metallurgical additives, and fusible alloys and solder.¹

B. Generalized Process Description

1. Discussion of Typical Production Processes

Bismuth is recovered mainly during the smelting of copper and lead ores. Exhibit 1 shows the extraction of bismuth-containing dust from copper-based sources. Bismuth-containing dust from copper smelting operations is transferred to lead smelting operations for recovery. At lead smelting operations, bismuth is recovered by one of two processes: the Betterton-Kroll Process (shown in Exhibit 2) and the Betts Electrolytic Process (shown in Exhibit 3).² Bismuth can also be recovered from other bismuth-bearing materials by the process shown in Exhibit 4. Exhibit 5 presents the flow diagram for the process used to refine the bismuth-lead alloy produced during either the Betterton-Kroll or the Betts Electrolytic Process.

2. Generalized Process Flow Diagram

Betterton-Kroll Process

As shown in Exhibit 2, the Betterton-Kroll process is based on the formation of high-melting compounds such as Ca_2Bi_2 and Mg_3Bi_2 that separate from the molten lead bullion bath and can be skimmed off as dross. During this process, magnesium and calcium are mixed with the molten lead to form ternary compounds (e.g., CaMg_2Bi_2). The ternary compounds rise to the surface when the lead is cooled to just above its melting point, forming a dross containing bismuth, calcium, magnesium, and lead, which is skimmed. Bismuth is recovered by melting the dross in a furnace, treating the dross with chlorine or lead chloride to remove the calcium, magnesium, and lead.³ The resulting chlorides are skimmed off the molten bismuth as a slag. The addition of air and caustic soda to oxidize any remaining impurities forms additional slag which can be disposed in conjunction with the slag from the blast furnace.⁴

¹ Stephen M. Jasinski, "Bismuth," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 30.

² "Bismuth," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1992, p. 238.

³ Laurence G. Stevens and C.E.T. White, "Indium and Bismuth," from Metals Handbook Volume 2. Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, Tenth ed., 1990, p. 753-754.

⁴ U.S. Environmental Protection Agency, Industrial Process Profiles for Environmental Use: Chapter 27, Primary Lead Industry, Office of Research and Development, July 1980.

EXHIBIT 1
BISMUTH COPPER SOURCES

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Waste, 1988, pp. 2-70 - 2-76.

EXHIBIT 2

BISMUTH BETTERTON-KROLL PROCESS

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Waste, 1988, pp. 2-70 - 2-76.

Betts Electrolytic Process

As shown in Exhibit 3, in the Betts Electrolytic Process the lead bullion with impurities is electrolyzed in a solution of fluosilicate and free fluosilicic acid with pure lead cathodes. The impurities, including bismuth, are retained in the form of a black anode slime. This slime is then scraped from the anode, washed, and partially dried prior to processing for bismuth. The recovery of bismuth is only one of several process end-product objectives in the treatment of the process residue. The primary objective is the fusion of the dried residues to produce a slag containing lead, arsenic, and antimony.⁵ The slimes are smelted and the resulting metal is cupelled, yielding a slag containing bismuth. The cupel slag is reduced and refined.⁶ One important difference between the Betts process and the Betterton-Kroll process is that in the Betterton-Kroll process, the lead bullion is purified prior to mixing with calcium and magnesium, while in the Betts process, the impurities are left in the lead bullion.⁷

Extraction From Bismuth Bearing Materials

As shown in Exhibit 4, bismuth also can be extracted from roasted tin concentrates and other bismuth-bearing materials by leaching with hydrochloric acid. After dilution of the acid leach, bismuth is precipitated as bismuth oxychloride. Further purification is achieved by redissolving the bismuth oxychloride in hydrochloric acid. The bismuth oxychloride is reprecipitated, dried, and reduced with carbon using soda ash flux to produce crude bismuth bullion.⁸

Refining

Exhibit 5 presents one method of bismuth refining in which the bismuth-lead alloy is mixed with caustic soda to form a purified metal mix. Zinc is added to the metal mix, which then undergoes Parkes Desilverization, a process used to recover gold and silver from softened lead bullion. The zinc combines with the molten bullion to form a skim with the gold and copper, which is then removed. More zinc is then added to form a silver skim layer which also is removed. Once the silver and gold are separated, they are sent for further processing and the recovered zinc can be recycled. More detailed description of Parkes Desilvering can be found in the description of lead processing found elsewhere in this report.

Following the desilverization process, chlorine is added to the resultant bismuth-bearing material which is then heated to 500° C. After heating, the impure bismuth is oxidized with air and caustic soda, producing 99.999 percent pure bismuth metal.

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

None Identified.

⁵ Funsho K. Ojebuoboh, "Bismuth-production, properties, and applications," JOM, 44, No. 4, April 1992, p. 47.

⁶ Laurence G. Stevens and C.E.T. White, 1990, Op. Cit., pp. 753-754.

⁷ Funsho K. Ojebuoboh, 1992, Op. Cit., p. 47.

⁸ Funsho K. Ojebuoboh, 1992, Op. Cit., p. 47.

EXHIBIT 3
BETTS ELECTROLYTIC EXTRACTION

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Waste, 1988, pp. 2-70 - 2-76.

EXHIBIT 4
RECOVERY FROM BISMUTH BEARING MATERIALS

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Waste, 1988, pp. 2-70 - 2-76.

EXHIBIT 5
BISMUTH REFINING

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Waste, 1988, pp. 2-70 - 2-76.

4. Beneficiation/Processing Boundary

The bismuth recovery process starts with materials obtained from the smelting of lead which is a minerals processing operation. Therefore, all of the wastes generated in the recovery process are categorized as mineral processing wastes. For example, even though leaching is typically considered to be a beneficiation operation, in this particular situation where it follows a minerals processing operation, waste from this step is categorized as mineral processing waste. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, please see the report for lead presented elsewhere in this background document.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Because bismuth is recovered as a byproduct of lead and copper ore production, mining wastes are addressed in the descriptions of the initial ore/mineral. For a further description of these wastes see the reports for copper and lead presented elsewhere in this background document.

2. Mineral Processing Wastes

The extraction methods used to recover bismuth (e.g., leaching, electrolysis) generate wastes including waste caustic sodas, electrolytic slimes, and waste acids. In addition, the following wastes are also generated during the processes described above. 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 low, medium, and high annual waste generation rates.

Extraction

Spent Caustic Soda. Low, medium, and high annual waste generation rates were estimated as 100 metric tons/yr, 6,100 metric tons/yr, and 12,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste stream may be recycled and may exhibit the characteristic of toxicity for lead. This waste is classified as a spent material.

Electrolytic Slimes. The slimes generated during this process are likely to be reprocessed. Low, medium, and high annual waste generation rates were estimated as 0 metric tons/yr, 20 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste stream may be recycled and may exhibit the characteristic of toxicity for lead. This waste is classified as a by-product.

Waste Acids. The waste acids generated are likely to be neutralized and discharged with waste water from the process. Low, medium, and high annual waste generation rates were estimated as 0 metric tons/yr, 100 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste stream may be partially recycled and may exhibit the characteristic of corrosivity. This waste is classified as a spent material.

Betterton-Kroll Process

Metal Chloride Residues. Chlorination generates magnesium and calcium chlorides. This waste stream has a reported annual waste generation rate of 3,000 metric tons/yr. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead.

Slag. The slag produced during this process contains magnesium, lead, and calcium. It is disposed with the blast furnace slag. Low, medium, and high annual waste generation rates were estimated as 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 for lead.

Betts Electrolytic Process

Spent Electrolyte. Low, medium, and high annual waste generation rates were estimated as 100 metric tons/yr, 6,100 metric tons/yr, and 12,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead.

Slag. Slag is generated from carbon reduction as shown in Exhibit 3.

Extraction From Bismuth-Bearing Materials

Spent Material. 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.

Wastewater. 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.

Waste acid solutions. As shown in Exhibit 4, these wastes are generated when the bismuth oxychloride is dissolved in hydrochloric acid. Low, medium, and high annual waste generation rates were estimated as 100 metric tons/yr, 6,100 metric tons/yr, and 12,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of corrosivity.

Bismuth Refining

As shown in Exhibit 5, the following wastes are associated with the bismuth refining process.

Spent soda solution. Low, medium, and high annual waste generation rates were estimated as 100 metric tons/yr, 6,100 metric tons/yr, and 12,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste stream may be recycled and may exhibit the characteristics of toxicity (lead) and corrosivity. This waste is classified as a spent material.

Excess chlorine. Low, medium, and high annual waste generation rates were estimated as 100 metric tons/yr, 150 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 reactivity.

Alloy residues. Low, medium, and high annual waste generation rates were estimated as 100 metric tons/yr, 3000 metric tons/yr, and 6000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead.

Lead and Zinc chlorides. Low, medium, and high annual waste generation rates were estimated as 100 metric tons/yr, 3000 metric tons/yr, and 6000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead.

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 (which may or may not be hazardous) and other lubricants.

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