ARSENIC

A. Commodity Summary

The most common source of arsenic is as a byproduct from the smelting of copper and lead concentrates as arsenic trioxide (As_2O_3). Arsenic trioxide is commonly converted to arsenic acid for use in producing arsenical wood preservatives, which accounted for 75% of the U.S. demand for arsenic in 1992.[1] Other uses include agricultural chemicals (16% of demand), glass manufacturing (4%), and other uses (2%). In addition, arsenic metal is produced by the reduction of arsenic trioxide and is used in nonferrous alloys and electronics, which accounted for 3% of demand in 1992.

China and Chile are the world's largest producers of arsenic trioxide, followed by Mexico and the Philippines. The United States imported over 13,000 metric tons of arsenic trioxide and over 500 metric tons of arsenic metal from China in 1992.[2] U.S. production of arsenic ceased in 1985 when ASARCO closed indefinitely its copper smelter and associated arsenic recovery plant in Tacoma, Washington, largely due to the increasing costs of complying with air quality standards.[3] Arsenic is no longer produced in the U.S., but three facilities, Hickson Corp. of Conley, GA, CSI of Harrisburg, NC, and Osmose Corp. of Memphis, TN, convert arsenic trioxide to arsenic acid for use in producing wood preservatives.[4]

B. Generalized Process Description

1. Discussion of Typical Production Processes

Arsenic trioxide (As_2O_3) is volatilized during smelting, concentrated in flue dusts, and extracted through distillation or roasting of the flue dusts to produce crude arsenic trioxide of minimum 95% purity.[5] This product can be refined through resublimation in a reverberatory furnace or through hydrometallurgical leaching methods to produce commercial-grade arsenic trioxide, known as white arsenic.[6]

2. Generalized Process Flow Diagram

Exhibit 1 presents a typical process flow diagram for the production and/or recovery of arsenic trioxide. As shown in the exhibit, vapor and gases laden with dust containing arsenic trioxide are liberated during smelting of copper (and lead) concentrates. Flue dust containing up to 30% arsenic trioxide is then roasted after a small amount of pyrite or galena is added to prevent the formation of arsenites and to promote formation of low-arsenic residue that can be recycled. The resulting high-arsenic fumes are passed through a series of brick chambers called kitchens (not shown in the diagram) that operate at progressively decreasing temperatures, from 220°C to 100°C or less, to condense the arsenic trioxide vapor

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[1] U.S. Bureau of Mines, Mineral Industry Surveys: Arsenic in 1992, Branch of Metals and the Branch of Data Collection and Coordination, June 1993, p. 4.

[2] Ibid.

[3] Loebenstein, J., The Materials Flow of Arsenic in the United States, U.S. Bureau of Mines Information Circular 9382, 1994, p. 2.

[4] U.S. Bureau of Mines, 1993, Op. Cit., p. 1.

[5] "Arsenic and Arsenic Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. III, 1992, pp. 626-628.

[6] U.S. Bureau of Mines, Mineral Facts and Problems, Bulletin 675, 1985, p. 45.

EXHIBIT 1

ARSENIC TRIOXIDE PRODUCTION PROCESS

Graphic Not Available.

Source: "Arsenic and Arsenic Alloys," 1992, Op. Cit., p. 627.

to concentrations of 90-95%. This crude trioxide is either pyrometallurgically refined through resublimation in a reverberatory furnace or hydrometallurgically refined through leaching. In the former method, the trioxide vapors pass through a settling chamber and then through about 40 additional kitchens to promote additional condensation, yielding white arsenic of 99-99.9% purity. Dust from the kitchens having 90% arsenic trioxide collects in baghouses and is reprocessed. In the latter method, arsenic trioxide fumes are pressure-leached in an autoclave using water or mother liquor. Arsenic trioxide dissolves and the resulting residue is reprocessed. The arsenic trioxide is recovered through vacuum-cooling to promote crystallization; arsenic trioxide is removed through centrifuging to yield white arsenic of 99% purity.[7]

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

The Bureau of Mines has investigated the recovery of arsenic from flue dusts from copper processing using an alternative method to distillation or roasting. Flue dusts were first leached with sulfuric acid and refinery-bleed solution to solubilize arsenic and copper. Arsenic was recovered as arsenic trioxide from the resulting leach liquor through reduction and precipitation using sulfur dioxide.[8] In 1981, Equity Silver Mines Limited in Houston, British Columbia began operating a leach plant to reduce arsenic levels in silver-gold-copper flotation concentrate. The concentrate was leached with caustic sulfide, producing a leach liquor containing most of the arsenic in the concentrate. The leached arsenic was originally recovered as calcium arsenate through oxidation and lime precipitation but was found to be not marketable. Full-scale plant tests were conducted in 1983 to produce a heavy metal arsenate thought to be marketable; however, the circuit was shut down in 1984 due to economic factors.[9]

4. Beneficiation/Processing Boundary

Since arsenic trioxide is recovered as a by-product of copper and lead smelting, please see the reports for lead and copper presented elsewhere in this background document for a description of where the beneficiation/processing boundary occurs for this mineral commodity, .

C. Process Waste Streams

The recovery of arsenic trioxide as a byproduct from copper and lead smelting constitutes primary mineral processing in the context of the Mining Waste Exclusion. In contrast, the manufacture of arsenic acid and arsenic metal from arsenic trioxide is considered to be chemical manufacturing and clearly has always been outside the scope of the Mining Waste Exclusion. Therefore, as there currently is no primary production of arsenic in the United States, there are no newly identified "mineral processing" wastes subject to the RCRA LDR program.

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[7] "Arsenic and Arsenic Alloys," 1992, Op. Cit., pp. 626-628.

[8] Gritton, K., D. Steele, and J. Gebhardt, "Metal Recovery from Copper Processing Wastes," presented at the Second International Symposium, Recycling of Metals and Engineered Materials, Williamsburg, Virginia, October 28-31, 1990, sponsored by the Minerals, Metals, & Materials Society, Warrendale, PA.

[9] Edwards, C., "The Recovery of Metal Values from Process Residues," Journal of Mines, June 1991, p. 32.

BIBLIOGRAPHY

"Arsenic and Arsenic Alloys." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. III. 1992. pp. 626-628.

Edwards, C. "The Recovery of Metal Values from Process Residues." Journal of Mines. June 1991. p. 32.

Gritton, K., D. Steele, and J. Gebhardt. "Metal Recovery from Copper Processing Wastes." Presented at the Second International Symposium, Recycling of Metals and Engineered Materials, Williamsburg, Virginia, October 28-31, 1990. Sponsored by the Minerals, Metals, & Materials Society, Warrendale, PA.

Loebenstein, J. The Materials Flow of Arsenic in the United States. U.S. Bureau of Mines Information Circular 9382. 1994. p. 2.

U.S. Bureau of Mines. Mineral Facts and Problems. Bulletin 675. 1985. p. 45.

U.S. Bureau of Mines. Mineral Industry Surveys: Arsenic in 1992. Branch of Metals and the Branch of Data Collection and Coordination. June 1993. p. 4.