

US EPA ARCHIVE DOCUMENT

MOLYBDENUM, FERROMOLYBDENUM, AND AMMONIUM MOLYBDATE

A. Commodity Summary

Almost all molybdenum is recovered from low-grade deposits of the mineral molybdenite, which is naturally occurring molybdenum disulfide (MoS_2), mined either from a primary deposit, or as a byproduct of copper processing.¹ In 1993, one mine extracted molybdenum ore, and nine mines recovered molybdenum as a byproduct. Two plants converted molybdenite concentrate to molybdic oxide, which was used to produce ferromolybdenum, metal powder, and other molybdenum compounds.² Exhibit 1 presents the names and locations of molybdenum mines and processing facilities.

EXHIBIT 1

SUMMARY OF MOLYBDENUM, MOLYBDIC OXIDE, AND FERROMOLYBDENUM PRODUCERS^a

Facility Name	Location
Cyprus-Climax - Henderson	Empire, CO
Cyprus-Climax	Fort Madison, IA
Cyprus-Climax	Clear Water, MI
Cyprus-Climax - Green Valley	Tucson, AZ
Cyprus-Climax	Bagdad, AZ
Kennecott	Bingham Canyon, UT
Kennecott	Salt Lake City, UT
Montana Resources Inc.	Butte, MT
Phelps Dodge	Chino, NM
San Manuel	San Manuel, AZ
San Manuel	Morenci, AZ
Thompson Creek	Chalis, ID
Thompson Creek	Langeloth, PA

^a - Personal Communication between ICF Incorporated and John W. Blossom, U.S. Bureau of Mines, October 1994.

Molybdenum metal is a refractory metal used as an alloying agent in steels, cast irons, and superalloys.³ Ferromolybdenum is an alloy of iron and molybdenum used primarily as an alternative additive in producing alloy steels, cast irons, and nonferrous alloys. The two most common grades of ferromolybdenum are low carbon- and high carbon ferromolybdenum. Ammonium molybdate is an intermediate in manufacturing both molybdenum metal and molybdic oxide, although it can also be sold as a product. Purified MoS_2 concentrate also is used as a lubricant.

B. Generalized Process Description

1. Discussion of Typical Production Processes

¹ J.W. Blossom, "Molybdenum," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, p. 849.

² J.W. Blossom, "Molybdenum," Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 114.

³ J.W. Blossom, 1992, Op. Cit., p. 847.

Molybdenum and molybdenum products, including ammonium molybdate, are made by roasting concentrated ore, followed by purification and/or reduction. Ferromolybdenum is typically produced by reaction of technical grade molybdc oxide and iron oxide with a conventional metallothermic process using silicon and/or aluminum as the reductant. These processes are described in greater detail below.

2. Generalized Process Flow Diagram

Molybdenum Metal and Ammonium Molybdate

Molybdenum metal and ammonium molybdate are made by roasting concentrated molybdenite ore, as shown in Exhibit 2. The concentration operations, which are not shown, include crushing, grinding, and flotation of either primary or copper ores. Molybdenite is recovered from either primary molybdenite or copper sulfide ore by flotation, after the ore has been crushed and ground to a suitable size. Several stages of grinding and refloatation concentrate the molybdenite in the primary ore to a 90 to 95 percent purity concentrate.⁴ The remainder of the concentrate is primarily silica.⁵ Copper, iron and lead are the impurities removed as tailings by this flotation process. Several sequential stages of flotation also are used for the copper ore, first to separate the gangue, and then the copper. The molybdenite concentration is usually 70 to 90 percent purity, when recovered from copper ores.⁶

Technical grade molybdc oxide, consisting of 90 - 95 percent MoO_3 , is produced by roasting molybdenite concentrate in a multiple hearth furnace at temperatures up to 650°C .⁷ Molybdenum concentrates may be leached with nitric acid prior to roasting to reduce the alkali concentrations in the concentrates.⁸ The roasting process removes sulfur and converts the sulfide to oxide. The flue gas contains products of combustion, SO_2 , and may contain rhenium or selenium. The SO_2 in the flue gas is converted to sulfuric acid (H_2SO_4).⁹ More information on the processing of the flue gas, and the production of sulfuric acid can be found in the Rhenium and Selenium sections of this document.

Pure molybdc oxide can be produced from technical grade molybdc oxide through sublimation and condensation or by leaching. In sublimation, the technical grade oxide is heated to approximately $1,100^\circ\text{C}$ in a muffle type furnace. The oxide is vaporized and carried in a stream of forced air through cooling ducts and the condensed oxide particles are collected in a fabric filter. The purified oxide contains greater than 99.5 percent MoO_3 . Technical grade oxide may also be purified by leaching with a hydrochloric acid-ammonium chloride solution (not shown). The impurities are dissolved and separated from the solid molybdc oxide by filtration. The pure oxide may be sold as a product, reduced to molybdenum metal powder, or used to produce various molybdenum chemicals.¹⁰

Ammonium molybdate is formed by reacting technical grade molybdc oxide with ammonium hydroxide and crystallizing out the pure molybdate. The ammonium molybdate may be sold as product, calcined to form pure molybdc oxide, or reduced to form molybdenum metal powder.¹¹

⁴ Ibid., p. 850.

⁵ "Molybdenum and Molybdenum Alloys," from Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XV, 1981, p. 670.

⁶ Blossom, J. W., 1992, Op. Cit., p. 850.

⁷ Ibid., p. 848.

⁸ U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Volume VI, Office of Water Regulations and Standards, May 1989, p. 3364.

⁹ "Molybdenum and Molybdenum Alloys," 1981, Op. Cit., p. 670.

¹⁰ U.S. Environmental Protection Agency, 1989, Op. Cit., p. 3364.

¹¹ Ibid.

Hydrogen is used to reduce ammonium molybdate or pure molybdc oxide to molybdenum powder, at 500-1150°C, in a boat- or tube-type furnace. The metal powder is sintered and cast into ingots or bars.¹²

Ferromolybdenum

Exhibit 3 illustrates the production of low carbon and high carbon ferromolybdenum. Low carbon ferromolybdenum is produced by mixing technical grade molybdc oxide, aluminum, ferrosilicon, iron oxide, limestone, lime, and fluorspar, and igniting the aluminum (not shown). A metal button and a slag are formed, allowed to solidify, and then are separated.¹³ High carbon content ferromolybdenum is made by reducing technical grade molybdc oxide, calcium molybdate, or sodium molybdate with carbon in the presence of iron in an electric furnace (not shown). The impurities from a slag which is discarded.¹⁴ Low carbon ferromolybdenum produced by the thermite process is more common than the high carbon alloy.

3. Identification of Novel or Distinct Process(es)

One researcher has investigated the separation and recovery of critical metals (including molybdenum) from mixed and contaminated superalloy scrap.¹⁵

4. Extraction/Beneficiation Boundaries

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 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 Section B.

Molybdenum Powder

EPA determined that for the production of molybdenum powder, the beneficiation/processing line occurs between the roasting and sublimation steps since leaching does not follow and because the molybdc sulfate is chemically roasted to pure molybdc oxide. 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

¹² "Molybdenum and Molybdenum Alloys," 1981, Op. Cit., p. 674.

¹³ U.S. Environmental Protection Agency, "Molybdenum," 1988 Final Draft Summary Report of Mineral Industrial Processing Wastes, 1988, p. 3-154.

¹⁴ Ibid., p. 3-154.

¹⁵ Hundley, G.L., and D.L. Davis, "Recovery of Critical Metals from Superalloy Scrap by Matte Smelting and Hydrometallurgical Processing," U.S. Bureau of Mines Report of Investigations 9390, 1991, p. 1.

initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

Ammonium Molybdate and Pure Molybdic Oxide

Based on a review of the process, there are no mineral processing operations involved in the production of either ammonium molybdate or pure molybdic oxide.

Ferromolybdenum

EPA determined that for ferromolybdenum, the beneficiation/processing line occurs at the furnace where the technical grade molybdic oxide and other materials are charged and undergo thermal reduction to form ferromolybdenum.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

The following wastes may be generated by extraction and beneficiation operations: gangue, flotation tailings, spent flotation reagents, and wastewater.^{16,17} The tailings from molybdenite concentration are not expected to exhibit any hazardous characteristics, but metal leaching and acid formation are possible.¹⁸

¹⁶ PEI Associates, Site Specific Data Summary Forms: Facilities Involved in the Extraction and Beneficiation of Ores and Minerals, Prepared for U.S. Environmental Protection Agency, Office of Research and Development, November 1986.

¹⁷ Weiss, Norman L., Ed. "Molybdenum," SME Mineral Processing Handbook, Volume II, Society of Mining Engineers, 1985, pp. 16-1 - 16-36.

¹⁸ U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-152.

2. Mineral Processing Wastes

Ammonium Molybdate Refining

Refining Wastes. Available data do not indicate that ammonium molybdate refining wastes exhibit any hazardous characteristics.¹⁹ Therefore, the Agency did not evaluate this material further.

Technical Grade Molybdc Oxide Production

Liquid Residues. Approximately 1,000 metric tons of liquid residues are generated annually in the United States. Available data indicate that this waste is potentially TC toxic. Potentially hazardous constituents include arsenic, cadmium, lead, and selenium.²⁰ The waste is not recycled. Liquids from the quench and scrubber towers/thickener contained the following constituents: arsenic - 60 ppm; cadmium - 1.2 ppm; chromium - 1.8 ppm; lead - 5.8 ppm; molybdenum - 100 ppm; and selenium - 32 ppm.²¹ Additional data is provided in Attachment 1. No other information on waste characteristics, or waste management was available in the sources listed in the bibliography.

Treatment Solids. Available data do not indicate that treatment solids exhibit any hazardous characteristics.²² Silicon was found at a concentration of 10 percent in solids from the quench and scrubber towers/thickener.²³ Therefore, the Agency did not evaluate this material further.

Solid Residues. Available data do not indicate that solid residues exhibit any hazardous characteristics (see Attachment 1).²⁴ Therefore, the Agency did not evaluate this material further.

Roaster Gas Blowdown Solids. Approximately 100 metric tons of roaster gas blowdown solids are generated annually in the United States. Available data do not indicate that this waste exhibits any hazardous characteristics.²⁵ Therefore, the Agency did not evaluate this material further.

Molybdc Oxide Refining Wastes. Approximately 2,000 metric tons of molybdc oxide refining wastes are generated annually in the United States.²⁶ This waste may exhibit the characteristic of toxicity for mercury,²⁷ and is not recycled.

Flue Dust/Gases. The flue gases produced during the roasting of molybdenite concentrates could contain volatile metals in the flue dust, in addition to the SO₂. These metals may include lead, zinc, tin and others.²⁸ Although no published information regarding waste generation rate 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 1,200 metric tons/yr, 270,000 metric

¹⁹ U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Volume I, Office of Solid Waste, August 1992, p. I-2.

²⁰ Ibid., p. I-6.

²¹ Ibid., Vol. II, p. 28-11.

²² Ibid., Vol. I, p. I-6.

²³ Ibid., Vol. II, p. 28-8.

²⁴ Ibid., Vol. II, p. I-6.

²⁵ Ibid.

²⁶ Ibid.

²⁷ U.S. Environmental Protection Agency, Technical background Document, Development of Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes, August 1989, p. 3-6.

²⁸ U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-153.

tons/yr, and 540,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for lead. This waste is not recycled.

Metal Refining

Refining Wastes. Available data do not indicate that metal refining wastes exhibit any hazardous characteristics.²⁹ Therefore, the Agency did not evaluate this material further.

H₂ Reduction Furnace Scrubber Water. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste (see Attachment 1). Therefore, the Agency did not evaluate this material further.

Ferromolybdenum Production

APC Dust/Sludge. This waste is generated by the baghouse or other APC device receiving the fumes from the ferromolybdenum furnace. Available data do not indicate that APC dust/sludge exhibits any hazardous characteristics.³⁰ Therefore, the Agency did not evaluate this material further.

Slag. This waste, formed in either the production of low carbon ferromolybdenum or high carbon ferromolybdenum, is not expected to exhibit any hazardous characteristics. The slag is usually discarded.³¹ Therefore, the Agency did not evaluate this material further.

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, 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.

²⁹ U.S. Environmental Protection Agency, 1992, Op. Cit., Vol. I, p. I-6.

³⁰ Ibid., p. I-4.

³¹ U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-154.

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